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A Monthly Journal of Research

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Dr. P. Sheel Memorial (Young Woman Scientist) Award Lecture
(October 25, 1997; at Bhubaneswar)

Plant tissue culture : the centre piece of plant biotechnology

RAJANI S. NADGAUDA

Tissue Culture Pilot Plant Division, National Chemical Laboratory, Pune - 8, India.

It is my pleasure to be here today to pay a tribute to late Prof. P. Sheel, who had an absorbing interest in diverse areas of science, which in his later years, was focused on rural development. Rural development is essential for the overall growth of the Indian Society, as, a large sectin of our population live in rural areas. In this context, application of plant tissue culture for crop plants and forest trees, has a definite role to play and can have an impact on rural development.

I am indeed honoured to be invited to give this year's Prof. Sheel Memorial Award Lecture, and I thank the Academy for this.

Plant Tissue Culture (PTC), is one of the important areas of Biotechnology. Biotechnology, in a broad sense covers all technologies developed by man, based on living organisms (microbial/plant/animal), for the benefit of mankind.

The development of plant tissue culture has its roots in the 'Cell Theory', independently proposed by Schleiden and Schwann (1838-39). Autonomy of the cell and its capacity to regenerate a whole plant (totipotency) were implicit in this theory.

The idea of cell tissue culture was put-forth by the German botanist, Haberlandt in 1902. All attempts to culture plant tissues were unsuccessful till the 1930's. In 1934, White could grow tomato roots in a liquid medium. Around 1939, the possibility of culturing plant tissues for indefinite periods was independently reported by White, Nobecourt and Gautheret.

Much of the progress in Plant Tissue Culture during the 1930's was on plant physiology, resulting in the discoveries of auxins (IAA etc.) and cytokinins (zeatin, ribosylzeatin, etc.). Skoog and Miller demonstrated the crucial role of auxin : cytokinin ratio in regulating morphogenesis.

Upto this time, the objective of tissue culture studies was ascertaining the possibility of culturing the cells indefinitely. Once this was achieved, attention was directed towards demonstrating totipotency and using this technique for the synthesis of secondary products.

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Somatic embryogenesis or asexual embryogenesis, as an alternative pathway of plant production, was first demonstrated by Reinert, in the late 1950's, in carrot. In 1965, Vasil and Hildebrandt reported that an isolated tobacco cell could divide and form a colony able to produce whole plants, demonstrating the totipotency of plant cells. Experimental proof of totipotency of plant cells had a catalytic effect in the progress of plant tissue culture and resulted in emergence and development of various branches.

In the 1980's the major thrust was on protoplast culture. The work on isolation and culture of protoplasts was initiated by Cocking in 1960. Protoplast fusion is now being used for obtaining interspecific and intergeneric hybrids, introduciton of organelles, uptake of microorganisms, transfer of foreign genomes (in part or in full) and the production of cytoplasmic hybrids.

Culture of floral organs was yet another landmark in plant tissue culture, achieved by Indian researchers Guha and Maheshwari (1962), who showed that the anthers of tobacco can be regenerated into haploid plants.

Cell and tissue culture systems are ideal for the enhanced production of secondary metabolites, through biotransformation, particularly where natural supplies are limited. They are also very useful in studies on the metabolic pathways and manipulation through recombinant DNA technology.

The foundation of modern micropropagation dates back to 1946 when Ball, pin-pointed which part of the meristem would regenerate into a whole plant. Later, shoot tips of virus infected dahlia and potato plants were also shown to be virus-free by Morel and Martin in 1950 who could produce healthy plants. Morel used shoot apices of orchids to obtain rapid clonal multiplication. Since then shoot tip culture has been the method of choice for obtaining virus free and true to type progenies.

In 1962, Murashige and Skoog, after very carefully analysing the nutritional requirements for tobacco tissue cultures, proposed a revised medium. This media formulation proved to be very useful for culturing a wide variety of plants.

Initially, success was obtained with micropropagation of ornamentals and herbaceous plants. Till the 1970's monocots and woody perennials were considered recalcitrant.

Propagation of mature trees is a prerequisite for capturing maximum gains through cloning. However, exudation of phenolics, microbial infestation and decline of regenerative capacity are the major problems faced at maturity when the desired characters are fully expressed.

In the 1980's the first report on micropropagation of a mature forest tree, teak, using meristem culture from NCL opened the avenue for tissue culture of forest trees. Since then a large number of woody perennials have been found amenable to micropropagation using meristem culture, axillary bud proliferation and somatic embryogenesis.

Today, micropropagation is enjoying the status of commercial success.

Somatic embryogenesis in cultured plant cells simulates zygotic embryogenesis.

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During the last decade, somatic embryogenesis is being viewed as an efficient, cost effective method, which facilitates scaling up operations, automation, encapsulation, fluid drilling, genetic transformation and cryopreservation.

This technology has vast potential for commercialization, and is also a valuable tool in the study of developmental biology. Somatic embryogenesis has been obtained in a large number of plant species. Although initiation, maturation and germination of these embryos is being studied in many species, high frequency regeneration, synchronous development and field planting of somatic embryo derived plants still pose difficulties. Characterization of the right stage of embryo development to obtain higher conversion rates is perhaps the most important factor.

Another application of plant tissue culture is induction and development of floral parts *in vitro*. This offers a great potential in studying the physiology of flowering and can also be used to produce hybrids. Recently, there are reports on the production of tomatoes and cucumbers *in vitro*.

Bamboos, the 'poor man's timber' is a much sought after industrial raw material of considerable economic importance. They have a peculiar behaviour of flowering and seeding at the end of very long vegetative growth phases followed by death of flowered clumps. The question, "Why bamboos wait so long to flower" (Jansen, 1976) has been intriguing scientists for long. Report on successful *in vitro* induction of flowering and seeding in bamboos poses another question "Why wait so long for bamboos to flower" (Nadgauda et al., 1993). So far, using tissue culture techniques, five reports are available, indicating drastic reduction of pre-flowering period from several decades to few months. This in turn raises a new set of questions :

- What are the problems and prospects of using *in vitro* induction of flowering for perennial seed production and hybridization ?
- What precisely is / are the factors responsible for induction of flowering *in vitro* ? Is it a cytokinin ? Is it (factor) specific to the medium ? Is it a physical factor ?, or is it combination of all these ?
- What are the factors controlling seeding under *in vitro* conditions ?

These questions are now being addressed in bamboos using the *in vitro* flowering system.

The quest for designing crop plants by novel methods and a realisation of the limitations of conventional breeding methods have led to some spectacular developments. These constitute the modern gene transfer/genetic engineering techniques. Presently many novel gene transfer systems are available for engineering the genetic make up of plants to suit human needs. Most successful among them are *Agrobacterium* mediated and direct gene transfer. Genetic transformation has been achieved for viral, insect/pest and herbicide resistance. Transgenic plants are also used for the production of oils, proteins, fibres, vaccines, pigments, secondary metabolites etc. The delayed senescene which improves the shelf life of fruits and vegetables has been a boon to these crops, since, the product is perishable.

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In the immediate future, the most important application of molecular biology to forest trees will be the characterization and isolation of markers linked to genes controlling desirable traits in superior candidate tress. This will be useful in the indentification and confirmation of superiority at an early age in micropropagated, vegetatively propagated and seed raised plants. A beginning has already been made by the manipulation of lignin metabolism in pulpwood tree species which would result in economic gains by reducing processing costs.

Thus the 20th century has witnessed the development of plant tissue culture from a concept to an important field of sicence and technology. In the initial stages, the growth of plant tissue culture as a discipline was very slow. Steadily it gained momentum and in the past two decades the development has been very rapid. Gradually there has been a shift from basic research to its applications.

At the turn of the century, virus eradication and micropropagation were the commercially successful stories. However, in the near future with the help of molecular biology and genetic engineering techniques, one can visualise the production of novel plant types with superior characteristics. The cell culture systems will be the future factories for the production of important secondary metabolites, vaccines and macromolecules.

Thus, it is evident that Plant Tissue Culture, has been, and will remain, *The Centre Piece of Plant Biotechnology.*

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The effect of polyamine bisoynthesis inhibitors on mycelial growth and mycotoxin production by *Aspergillus terreus*

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Abstract *Aspergillus terreus* strains were screened for efficacy of polyamine biosynthesis inhibitors (MGBG and CHA) in the control of patulin and terreic acid production. Terreic acid production was completely inhibited by CHA when used at 5 mM. Both CHA and MGBG inhibited the patulin production by 55 and 43% respectively at 5 mM. However, both the compounds were responsible for marginal inhibition of mycelial growth in two strains of *A. terreus*.

(**Keywords** : *Aspergillus terreus/patulin/terreic acid/polyamines/mycelial growth)*

Polyamines (PAs) have been shown to be involved in growth and developmental processes in a wide range of organisms, including fungal systems[1,2]. The diamine putrescine (Put) is synthesized directly from ornithine decarboxylation or indirectly from arginine decarboxylation by ornithine and arginine decarboxylase (ODC and ADC), respectively[1]. PAs, spermidine (Spd) and spermine (Spm) are derived from Put by the addition of the aminopropyl groups (donated by decarboxylated S-adenosylmethionine) to Put by Spd and Spm synthases, respectively[1]. Both these pathways (ODC and ADC) operate in bacteria and plant cells[2-4]. By contrast, only the ODC pathway is involved in the synthesis of Put in mammals[3] and in most fungal systems[2,4,5]. Since most of the fungi have only ODC pathway for PA biogenesis and since PAs are essential for normal growth and differentiation[4], the specific inhibition of fungal PA biosynthesis using ODC inhibitors, notably difluoromethylornithine (DFMO) has been exploited for the control of plant diseases[4-6]. Though, considerable work has been undertaken to control various plant diseases by PA biosynthesis inhibitors without affecting the host plant growth and development[4,6-9], studies have not been undertaken to assess efficacy of these inhibitors in management of vegetative growth and mycotoxin produciton by mycotoxigenic strains of *Aspergillus terreus* Thom; commonly found on various agricultural products, including spices, animal feed and fodder. *A. terreus* produces mycotoxins such as diabetogenic terreic acid and patulin that are responsible for causing haemorrhages in the lung and brain when injested[10]. Therefore, in a view to curtail the incidence of mycotoxins, it was considered worthwhile to study the effect of two PA biosynthesis inhibitors, methylglyoxal *bis* (guanylhydrazone) (MGBG, an inhibitor of S-adenosylmethionine decarboxylase) and *bis* (cyclohexylammonium) sulphate (CHA, an inihibitor of Spd synthase) on the mycelial

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growth and mycotoxins production by two different strains of *A. terreus*, each one is responsible for the production of terrreic acid and patulin.

Different concentrations of MGBG and CHA stocks, freshly prepared with sterilized double distilled water, were added to 50 ml sterilized minimal medium[11] in 250 ml Erlenmeyer flasks to give final concentrations of 1.0, 2.5 and 5.0 mM under aseptic conditions. Monosporic cultures of 6-d-old patulin - producing strain of *A. terreus* (isolated from *Curcuma longa* L. corm), and a terreic acid producing strain (isolated from *Zinziber officinale* Roxb. rhizome) from Czapek yeast agar slants[12] were inoculated to the minimal medium. Uninoculated flasks were served as controls. These were incubated at 28±1°C for 15 days. The effect of MGBG and CHA on biomass (dry wietght) and mycotoxin (patulin and terreic acid) production was recorded at the end of incubation period. To measure the fungal growth in liquid medium, cultures were heated to 121°C for 30 s to kill the spores and vegetative mycelium. The mycelial mats were then separated from the residual culture broth, washed with distilled water and dried at 80°C for 16 h before weighing. The final pH of the culture filtrates was also recorded. Terreic acid and patulin from the respective culture filtrates were extracted with chloroform and analysed qualitatively[13] and quantitatively[14,15].

The PA biosynthesis inhibitors under the study exhibited varied toxicity against both strains of *A. terreus*. Both CHA and MGBG were strong inhibitors of terreic acid production but moderate in their toxicity against patulin production even when used at maximum concentration (5 mM). However, these compounds had little effect on mycelial growth of either strain of *A. terreus*. MGBG inhibited the terreic acid production by 85%. Also, the final pH of the culture filtrates was also increased to 6.4. In contrast, CHA was responsible for 96% inhibition of terreic acid producion even at 2.5 mM concentration and completely inhibited the toxin production when used at 5.0 mM (Table 1). DFMO was found to be weak inhibitor of both terreic acid production and vegetative growth of *A. terreus* (Unpublished results).

CHA and MGBG moderately inhibited the patulin production and marginal inhibitory effect on mycelial growth. CHA inhibited the patulin porduction by ca. 55% and vegetative growth by 34% at 5.0 mM, while MGBG showed 43% inhibition of patulin production (Table 2). DFMO was found to be weak inhibitor and showed only marginal inhibition of both mycelial growth and patulin production even at 5.0 mM. (data not shown).

From these preliminary results, it is evident that the PA biosynthesis inhibitors infuluenced the mycelial growth and mycotoxin production by both the strains of *A. terreus*; this may be due to the possibility of changes in the activity of specific PA biosynthesis enzymes and PA titers followed by inhibitor treatments, which may be responsible for a rapid change in the physiology of fungi. However, further work is needed in this direction. The inhibitory effect of PA biosynthesis inhibitors, including MGBG and CHA on growth and PA metabolism of several phytopathogenic have been studied[4,7-9].

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Table 1– Effect of PA biosynthesis inhibitors on mycelial growth and terreic acid production by *Aspergillus terreus* (Terreic acid strain).

PA inhibitor treatment (mM)	pH	Dry weight mg/ml	Terreic acid* ppb
MGBG			
1.0	6.0	13.1	3.2
2.5	6.2	12.8	3.0
5.0	6.4	11.5	2.8
CHA			
1.0	6.0	11.8	15.0
2.5	6.2	11.5	0.7
5.0	6.2	9.4	-
Control	5.0	13.1	18.0

0.01 O.D. = 10 ppb
*An average of two determinations of colorimetric analyses.

Table 2– Effect of PA biosynthesis inhibitors on mycelial growth and patulin production by *Aspergillus terreus* (Patulin strain).

PA inhibitor treatment (mM)	pH	Dry Weight mg/ml	Patulin* ppb
MGBG			
1.0	7.0	11.3	105.0
2.5	7.0	10.7	99.0
5.0	7.0	6.3	69.0
CHA			
1.0	6.8	11.0	102.0
2.5	6.8	10.7	83.0
5.0	6.5	10.0	53.0
Control	7.0	15.5	120.0

0.01 O.D. = 10 ppb
*An average of two determinations of colorimetric analyses.

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Effect of soil amendment of *Clerodendrum aculeatum* and *Clerodendrum fragrans* on disease incidence of pigeonpea wilt

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Abstract Plants of pigeonpea (*Cajanus cajan*) were treated with dry leaf powder of *Clerodendrum aculeatum* and *Clerodendrum fragrans* by soil amendement in two different sets respectively under glass house conditions. Culture filtrate of *Fusarium oxysporium udum* was inoculated in all the control and treated sets. A total of five soil amendment (two pre-inoculation and three post-inoculation) treatments were given throughout the experiment. After sixty days of inoculation, 30% to 40% disease incidence was recorded in treated sets, where as control plants showed 60% to 65% disease incidence. Due to decrease in disease incidence, general increase in various morphological parameters was also achieved in treated sets. The best result in protecting pigeonpea crop from wilt pathogen and an increase in yield of around 4 times was obtained by soil amendments with *Clerodendrum aculeatum* under glass house conditions.

(**Keywords**: *Clerodendrum* / soil amendment / pigeonpea/wilt)

Wilt is the most destructive disease of pigeonpea in India. The causal fungus *Fusarium oxysporum udum* is sparophytic in nature, and can survive in soil for years and can also withstand widely varying adverse conditions including a pH range of 4.6 to 9.0 and soil temperatures of up to 35°C[1]. Several methods, such as cultural practices, crop rotation, mixed cropping, green manuring and use of various fungicides have been recommended for the control of this pathogen[2].

However, an alternative method of controlling disease incidence and increasing productivity has been tried in this experiment. The aqueous extract or dry leaf powder mixture of leaves of the plants of *Clerodendrum aculeatum* and *Clerodendrum fragrans* were found to be effective against certain virus diseases which occur naturally or are mechanically transmitted[3,4] These plant products were referred to as resistance inducers by Verma[5].

In the present communication, effort has been made to minimize the disease incidence of wilt by using dry powder leaves of *Clerodendrum aculeatum* and *Clerodendrum fragrans* as soil amendment.

Three sets of 10" fifty pots, each having two replicates twenty five pots were filled with compost soil. Set I of pots labelled T1 and T2 was used as control set where no amendment to the soil was made. In the Set II of pots labeled T3 and T4, the soil was treated with dry powdered leaves of *Clerodendrum fragrans* at the rate of 20 gms per kg. In the Set III of pots labelled T5 and T6, dry leaf powder of *Clerodendrum aculeatum* was

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mixed thoroughly with the soil at the rate of 20 gms per kg.

After 16 hours of soil amendment, seeds of pigeonpea were sown in each pot. An adjustment was made after germination by retaining only two seedlings of same vigor in each pot. The second pre-inoculation treatment was given in both sets II and III, when the seedlings were 10 days old.

Fusarium oxysporum udum culture was obtained from IARI, New Delhi. The fungus was multiplied on potato dextrose broth in 250ml flasks. The contents were filtered through filter paper (Whattman No. 1) after 10 days of inoculation when broth medium was full of mycelial mat. Pooled filtrate was centrifuged at 12100 g for 20 minutes and used as culture filtrate. 50 ml of this culture filtrate was used for soil inoculation of each pot.

After fifteen days of second pre-inoculation treatment, all control as well as treated plants were challenge inoculated with culture filtrate *Fusarium oxysporum udum*.

The third, fourth and fifth treatment (by soil amendment with the leaf powders) were given to sets II and III (T3, T4, T5 and T6) after 30, 40 and 50 days of sowing respectively. Plants of control sets were amended with same amount of compost soil at the same time.

All the plants were kept under glass house conditions. Weeding and other normal agricultural practices were maintained through out the experiment. Plants were regularly observed for development of symptoms.

After 20 days of inoculation, mild chlorotic spots appeared on the leaves of 2-3 plants of set I. Characteristic drying of stem and leaves was observed in 48% plants after 30-40 days of inoculation. After 60-70 days of inoculation, maximum disease incidence of 56% to 60% was recorded (Table 1).

Most plants of set I showed varying degrees of disease symptoms ranging from very mild chlorotic spots, distinct chlorotic spots, partial drying to total wilting of shoots. Wilting of leaves and stems along with general decrease in all the growth parameters was observed.

The appearance of disease symptoms was delayed by 8-10 days in plants of set II and III. In the T3 and T4 replicates of set II, only 20% to 40% disease incidence was recorded even after 70 days of inoculation. Initially, very faint chlorotic spots were observed on 4-5 plants only which later developed on 10 out of the 25 plants of this set.

In set III, the effect was more pronounced. In T5 and T6 replicates, the disease incidence was only 12% to 16% even after 30 days of inoculation.

In both sets II and III, the onslaught of disease was quite slow as compared to set I. In between 30 to 60 days after inoculation, the disease spread rapidly. An increase of 36% to 56% in severity of existing symptoms was observed in set I. During the same time period the disease incidence on plants of sets II and III increased from 20% to 40% and from 16% to 32% respectively. However, no increase was observed in the disease incidence after 40 days of inoculation.

A comparative study of various morphological parameters between set I and the

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Table 1– Observations on disease incidence and symptoms severity in pigeonpea receiving treatment of *Clerodendrum aculeatum*, *Clerodendrum fragrans* and inoculum of *Fusarium oxysporium udum* under natural conditions.

Particulars	Number of days after inoculation				
	20	30	40	60	70
Control set I (Sub Set T1)					
No. of infected plants	2	9	12	14	14
Disease incidence %	8	36	48	56	56
Symptoms severity	+	++	+++	++++	++++
(Sub Set T 2)					
No. of infected plants	3	11	13	15	15
Disease incidence %	12	44	52	60	60
Symptoms severity	+	++	+++	++++	++++
Treated set II (Sub Set T 3)					
No. of infected plants	0	5	10	10	10
Disease incidence%	-	20	40	40	40
Symptoms severity	-	+	++	+++	+++
(Sub Set T 4)					
No. of infected plants	0	4	10	10	10
Disease incidence %	-	16	40	40	40
Symptoms severity	-	+	++	+++	+++
Treated set III (Sub Set T 5)					
No. of infected plants	0	3	7	7	7
Disease incidence %	-	12	28	28	28
Symptoms severity	-	+	+	++	++
(Sub Set T 6)					
No. of infected plants	0	4	8	8	8
Disease incidence %	-	16	32	32	32
Symptoms severity	-	+	++	++	++

1. Data represents average of 25 plants from each sub-set.
2. - No symptoms of the disease apparently present.
3. + Very mild chlorotic spots on lower leaves present.
4. ++ Distinct chlorotic spots and partial wilting of leaves.
5. +++ Severe wilting of leaves with partial drying of shoots.
6. ++++ total wilting of leaves and stems.

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Table 2– Observations on morphological parameters and yield from pigeonpea plant.

Particulars	Control set I		Treated set II		Treated set III	
Sub Sets-	T1	T2	T3	T4	T5	T6
Average shoot (in cms)	34.00	30.80	60.00	61.10	62.00	61.00
Average root length (in cms)	16.26	15.30	22.00	21.30	24.00	24.00
Average no. of root nodules per plant	11.00	12.00	20.00	20.00	25.00	27.00
Average no. of flowers per plant	3.00	3.00	9.00	8.00	14.00	16.00
Average no. of pods per plant	7.00	8.00	22.00	24.00	36.00	35.00
Fresh weight per plant (in gms)	6.00	6.80	15.00	15.50	24.60	23.00
Dry weight per plant (in gms)	1.65	1.66	5.00	5.20	7.80	7.00
Disease incidence after 60 days of inoculation %	58.00	60.00	40.00	40.00	30.00	32.00
Control over disease incidence (C - T) x 100 / C	-	-	31.03	33.33	48.27	46.66

Data represent average of twenty five plants from each subset.
Observations were recorded after seventy days of inoculation.

sets II and III showed that various morphological parameters increased markedly in plants of sets II and III over the set I. (Table 2).

Number of root nodules and shoot length doubled in sets II and III, while number of flowers per plant and number of pods per plant increased 300% and 500% in sets II and III respectively, as compared to set I. The disease incidence was contained up to 31% to 33% and 46% to 48% respectively in sets II and III as compared to set I. Thus the effect was more pornounced on amendment of soil with *Clerodendrum aculeatum*.

In present experiment, effect of *C. fragrans* and *C. aculeatum* on *Fusarium oxysporium udum* was probably associated with fungistatic effect of above leaf extracts. Duration of the fungistatic state against subsequent infection, was of short duration, therefore periodic repetition was required. Prophylactic treatment during seedling stage probably plays a vital role in preparing the host plant in resisting subsequent infections. The induction of fungistatic state, by soil amendment is not a permanent feature and the effect is pathogen specific, because in fields, where natural occurrence of pathogen takes place, effect of the same amendments was reduced perhaps due to multiple infections. Therefore, further work is required on the fields to prepare a potent amendment against incidence of this pathogen in crops.

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Complex formation equilibria of 5-fluorouracil with proton and metal ions

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Abstract Potentiometric study of complex formation of 5- fluorouracil and metal ions have been done in aqueous, methanol- water, ethanol-water, isopropanol-water and dioxan-water medium at constant mole fraction (0.24) of organic solvent in 0.15 mol dm^{-3} NaCl ionic strength at 25°C. The stability sequence $Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ was observed in each aqueous organic medium.

(**Keywords** : 5-fluorouracil/protonation constants/ formation constants/metal ions)

The interaction of transition metal ions with nucleic acid constituents has become an interesting area of study due to their biological significance[1] and potential chemotherapeutic significance[2]. A survey of literature shows that scanty data is available on complex formation equilibria of uracil and substituted uracils with proton and metal ions in mixed aqueous organic solvents[3]. 5-Fluorouracil can replace uracil in RNA and together with 5-fluoro-2'-deoxyuridine is employed in tumour chemotherapy. In view of above facts, it is thought worthwhile to study the complex equilibria of 5- fluorouracil in different aqueous organic media. The present report describes a potentiometric study on complexation of Co^{++}, Ni^{++}, Cu^{++} and Zn^{++} ions with 5-fluorouracil.

The purity of 5-fluorouracil (SISCO grade) was checked potentiometrically and its solution was prepared in glass distilled water. All other chemicals were of A.R. grade. Total volume in each case was 20 ml. An EC digital pH meter with combined glass and calomel electrode assembly was used for pH measurements (accuracy±0.01) in potentiometric titrations against 0.1 N NaOH. The pH titration technique of Irving and Rossotti[4] was used to determine protonation constant of 5-fluoro-uracil and formation constants of metal-5-fluorouracil complexes. The pH values in aquo-organic mixture were corrected[5]. The following mixtures (a) 1×10^{-2}M HCl, (b) $a+2 \times 10^{-3}$M 5-fluorouracil and (c) $b+4 \times 10^{-4}$M metal ions were prepared at constant mole fraction (0.24) of organic solvent in aqueous, methanol-water (42.5:57.5%, v/v), ethanol-water (51,8;48.2%, v/v), isopropanol-water (58.6 : 41.4% v/v) and dioxan-water (61.2 : 38.8% v/v) mixture at ionic strength of 0.15M NaCl at 25°C and titrated against 0.1 N NaOH potentiometrically. The titration curves for acid, acid+ligand and acid+ligand+metal ion were drawn and are shown only for ethanol-water mixtures (Fig. 1). The protonation constant (log K^{H}_{1}) and metal-ligand stability constants (log β_2) were calculated by various computational methods[6] and average values are reported in Table 1.

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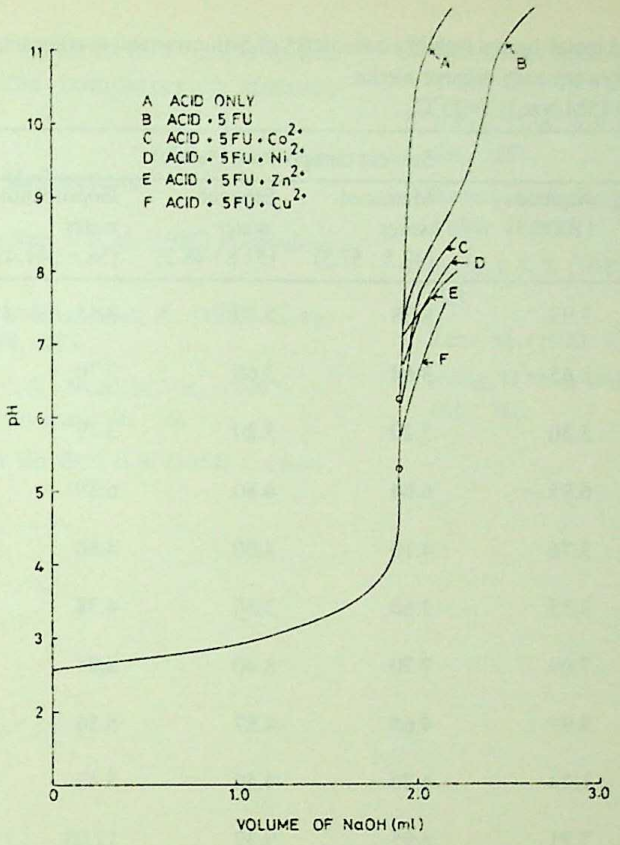

Fig. 1 --Titration curves for 5-fluorouracil (5-FU) and its metal complexes in ethanol-water medium.

5-Fluorouracil released only one proton in the pH range 6.5-11 corresponding to the equilibria I $\rightleftharpoons$ II and the protonation constant log K_1^H value (7.93) in aqueous medium is in agreement with previously reported value (pK= 7.8)[7]. The presence of electron-withdrawing halogen(F) group at 5-position exerts an inductive as well as mesomeric effect and consequently results in lower dissociation constant value compared to uracil[8] (pK=9.17). The log K_1^H value for various aqueous organic mixtures follow an order: dioxane-water > isopropanol-water ~ethanol-water ~methanol-water> water. Born equation[9] predicts that creation of change in the medium of low dielectric constant is an unfavourable process and thus the equilibria I $\rightleftharpoons$ II should be unfavourable and hence results in greater log K_1^H value in aqueous-organic mixtures.

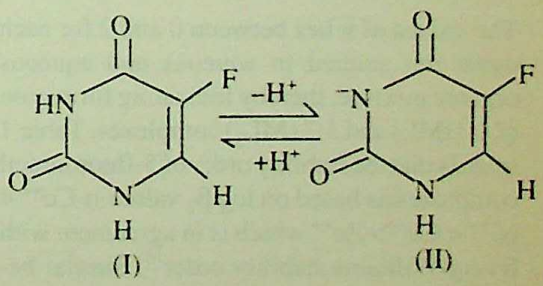

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Table 1 – Proton-ligand and metal-ligand stability constants* of 5-fluorouracil at constant mole fraction (0.24) of organic solvent in aqueous organic media.
Ionic strength = 0.15M NaCl; T=25°C.

		Solvent composition (% v/v)				
Cation	Constant	Aqueous (100%)	Methanol-water (42.5 : 57.5)	Ethanol-water (51.8 : 48.2)	Isopropanol-water (58.6 : 41.4)	Dioxan-water (61.2 : 38.8)
H^+	$\log K_1^H$	7.93	8.38	8.39	8.43	8.79
Co^{2+}	$\log K_1$	3.65	3.64	3.60	3.70	3.96
	$\log K_2$	3.30	3.20	3.20	3.19	3.50
	$\log \beta_2$	6.95	6.84	6.80	6.89	7.46
Ni^{2+}	$\log K_1$	3.76	4.10	4.60	4.60	5.23
	$\log K_2$	3.33	3.60	3:80	4.38	4.44
	$\log \beta_2$	7.09	7.70	8.40	8.98	9.67
Cu^{2+}	$\log K_1$	3.97	4.65	4.87	5.56	5.74
	$\log K_2$	3.74	4.30	4.50	5.47	5.56
	$\log \beta_2$	7.71	8.95	9.37	11.03	11.30
Zn^{2+}	$\log K_1$	3.80	3.80	3.88	3.95	4.02
	$\log K_2$	3.45	3.45	3.43	3.65	3.66
	$\log \beta_2$	7.25	7.25	7.31	7.70	7.68

*Limits of error of $\log \beta_2$ values are ± 0.04

The values of $\bar{n}$ lies between 0 and 2 for each metal ion studied in aqueous and aqueous organic mixture, thereby indicating formation of 1:1(ML) and 1:2 (ML_2) complexes. Table 1 reveals that the stability order of 5-fluorouracil complexes as based on $\log \beta_2$ values is $Co^{++} < Ni^{++} < Cu^{++} > Zn^{++}$ which is in agreement with Irving-Williams stability order[10]. Similar behaviour has also been noticed in case of Cu^{++}/Ni^{++} - 5- bromouracil and 5-iodouracil systems[3]. Further the data in Table 1 indicate that $\log \beta_2$ values are greater in dioxan-water medium as compared to aqueous medium[3] as expected. This may be due to the fact that solvation number of metal ions is more in aqueous medium as compared to the aqueous-

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organic medium which in turn results in the formation of weak complexes in aqueous medium.

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Studies of some mixed-ligand derivatives of hydroxo (aqua) bis-(acetoacetylarylamido) lanthanum (III) with 8-hydroxyquinoline/ 8-hydroxyquinoline-4-(phenyl) sulphonamides

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Abstract Some new mixed-ligand complexes of lanthanum(III) of the composition [La(A-A)$_2$(L-L)], where (A-A)H = acetoacetanilide, *o*-acetoaceto-toluidide or o-acetoacetanisidide and (L-L)H = 8-hydroxyquinoline or 8-hydroxyquinoline-4-(phenyl) sulphonamide. These mixed-ligand chelates have been obtained by the interaction of hydroxo (aqua) bis (acetoacetanilido)-, hydroxo (aqua) bis (o-acetoa-cetotoluidido)-, and hydroxo (aqua) bis (o-aceto-acetanisidido)-lanthanum (III) with the said ligands. The metal chelates so obtained have been characterized by elemental analyses, electrical conductances, magnetic measurements, electronic and infrared spectral studies. An octahedral structure has been proposed for these complexes.

(**Keywords** : electronic & IR spectra/magnetic studies/mixed ligand complexes/lanthanum (III))

The chelating behaviour of 8-hydroxy-quinoline/8-hydroxyquinolinesulphonamide is well established[1]. Acetoacetylarylamide viz., acetoacetanilide, o-acetoacetanisidide or o-acetoacetotoluidide is comparable to acetylacetone in its complexing ability[2]. The chemistry of β-diketone complexes has aroused much interest in many areas, viz., spectral studies, solvent extraction, column and thin layer chromatography, N.M.R. shift reagent, laser technology and in the polymer industry[3]. Some lanthanide ions when combined with heterocyclic β- diketone, viz., 4-acyl-3-methyl-1-phenyl-2-pyrazoline-5-ones exhibit excellent fluorescence[4] which provide an opportunity for studying their applications in analysis and optical materials. In view of the potential ligating behaviour and biological importance of pyrazolone based heterocyclic β-diketone, Maurya *et al.*[5] have recently reported the isolation and characterization of several lanthanum(III) chelates involving schiff bases derived from such heterocyclic β-diketones.

A literature survey on mixed-ligand β-diketone complexes reveals that there is no report on mixed-ligand complexes involving acetoacetarylamides and 8-hydroxyquino-lines/8-hydroxyquinoline sulphonamides. It was, therefore, thought worthwhile to synthesize and characterize the hitherto unreported mixed-ligand chelates of lanthanum(III) with some acetoacetylar-lyamides, such as, acetoacetanilide (AANH), o-aceto-acetotoluidide (OAATH) or o-aceto-acetani-sidide (OAAANH), and 8-hydroxy-quinolinesulphonamide, viz., 8-hydroxy-quinoline-4-(phenyl) sulphonamide. The structures of the chelating ligands are shown in Fig. 1.

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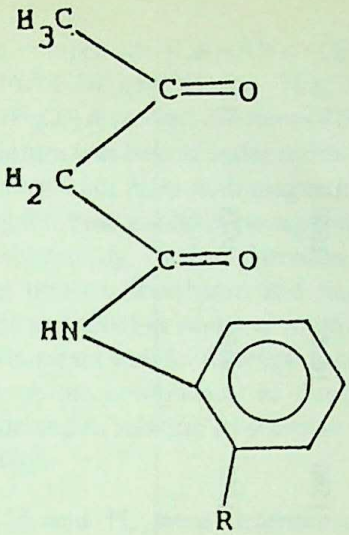
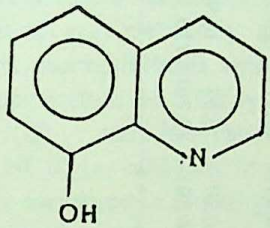


(acetoacetylarylamides)

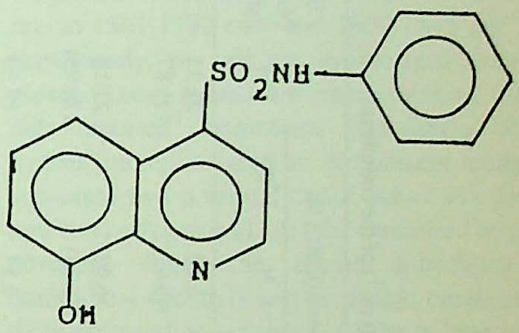
R = H, acetoacetanilide.

R = CH_3, o-acetoacetotoluidide

R = OCH_3, o-acetoacetanisidide.



(HQ)



(HQPS)

Fig. 1 – Structure of ligands.

$La(NO_3)_3.6H_2O$ (B.D.H. Chemical Bombay), acetoacetanilide, o- acetoacetotoluidide and o-acetoacetanisidide (Aldrich Chemical Company, U.S.A.), 8-hydroxyquinoline (Ward Blenkinshop Co. Ltd., London), chlorosulphonic acid (B.D.H. Chemicals, Poole, England), and aniline (Sarabhai M. Chemicals, Baroda) were used as supplied. 8-Hydroxyquinoline (4-phyenyl) sulphonamide was prepared by the reported method[1]. The parent compounds, $[La(AAN)_2(OH)(H_2O)]$, $[La(OAAT)_2(OH)(H_2O)]$ and $[La(OAAAN)_2(OH)(H_2O)]$ used in the present investigation were prepared by following the method of Dutt and Sur[6]. Their decomposition temperatures are 205, 150 and 159°C, respectively.

A stoichiometric amount (0.01 mol) of 8-hydroxyquinoline or 8- hydroxyquinoline-4-(phenyl) sulphonamide dissolved in sufficient volume of ethanol (~15ml) was added to the solution (~20 ml) of the freshly prepared

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Table 1 – Analytical data and important ir spectral bands (cm^{-1}) of the complexes.

Sr. No.	Compound (Empirical Formula)	Found (Calc.) %				La	ν (C=O) (Acetyl carbonyl)	ν (C=O) (Amide carbonyl)	ν (C=N)	ν (C=O)
		C	H	N	S					
1.	[La $(AAN)_2$(HQ)] ($C_{29}H_{26}N_3O_5LA$)	54.62 (54.81)	4.27 (4.69)	6.42 (6.61)	–	21.32 (21.87)	1567	1600	1633	1102
2.	[La $(OAAT)_2$(HQ)] ($C_{31}H_{30}O_5N_3LA$)	56.41 (56.11)	5.27 (4.52)	6.08 (6.33)	–	21.18 (20.95)	1581	1614	1660	1108
3.	[La $(OAAAN)_2$(HQ)] ($C_{31}H_{30}O_7N_3LA$)	53.30 (53.53)	4.09 (4.32)	6.37 (6.04)	–	19.50 (19.98)	1570	1600	1650	1105
4.	[La $(AAN)_2$ (HQPS)] ($C_{35}H_{31}N_4O_7$ SLa)	53.38 (53.17)	3.62 (3.92)	7.25 (7.09)	4.25 (4.05)	17.97 (17.58)	1575	1608	1635	1108
5.	[La $(OAAT)_2$ (HQPS)] ($C_{37}H_{35}N_4O_7$ SLa)	54.39 (54.28)	4.65 (4.28)	6.42 (6.84)	3.69 (3.91)	17.10 (16.98)	1580	1615	1640	1112
6.	[La $(OAAAN)_2$ (HQPS)] ($C_{37}H_{35}N_4O_9$ SLa)	52.07 (52.24)	4.37 (4.12)	6.20 (6.59)	3.52 (3.76)	16.92 (16.34)	1582	1610	1645	1115

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parent compounds $[La(AAN)_2(OH)(H_2O)]$, $[La(OAAT(OH)(H_2O)]$ or $[La(OAAAN)_2(OH)(H_2O)]$ dissolved in acetone. The resulting mixture was heated under reflux for 1 h at 80°C over a hot plate with magnetic stirring. During this time a solid mass separated out. It was isolated by suction filtration, washed several times with ethanol and finally with acetone and dried *in vacuo* at room temperature to constant weight. Attempts to crystallize a few of the compounds in dimethyl formamide and in mixture of solvents were unsuccessful.

C,H and N, were determined microanalytically at C.D.R.I., Lucknow, The lanthanum content of each of the complexes was determined gravimetrically as La_2O_3[7]. The magnetic susceptibilities were measured at room temperature on a Gouy balance, using mercury(II) tetrathiocyanatocobaltate(II), $Hg[Co(NCS)_4]$ as calibrant. Molar conductances were measured in dimethylformamide on a Toshniwal conductivity bridge. Infrared spectra (4000-450 cm^{-1}) of the ligands and complexes were recorded as nujol mulls on a FT-IR spectrophotometer. Electronic spectra of the complexes were recorded in 10^{-3}M solution in dimethylformamide on a Shimadzu model, UV-160 spectrophotometer.

The lanthanum(III) mixed-ligand chelates with ligands under study were prepared according to the following scheme-

$$[La(AA)_2(OH)(H_2O)] + (L\text{–}L)H \xrightarrow[\text{Reflux}]{EtOH/Me_2CO} [La(AA)_2(L\text{–}L)] + 2H_2O$$

where (L-L)H = 8-hydroxyquinoline or 8-hydroxyquinoline-4- (phenyl) -sulphonamide, and (A-A)H = AANH, OAATH or OAAANH.

Analytical data and important IR spectral bands of complexes are given in Table 1. The resulting complexes are non-hygroscopic, air stable coloured solids (Table 2). The decomposition temperatures of these complexes are given in Table 2.

The significant absorption bands due to coordinated acetoacetanilide, o-acetoacetotoluidide and o-acetoacetanisidide are ν(C=O) (acetyl carbonyl) and ν(C = O) (amide carbonyl) and these have been observed in the region 1567-1582 cm^{-1} and 1600-1615 cm^{-1}, respectively, in all the synthesized complexes. These results are comparable to the data reported[8] elsewhere. The ligand 8-hydroxyquinoline used in the present study possesses two potential donor sites : (1) the hydroxyl oxygen and (ii) the quinoline ring nitrogen, while the ligand 8-hydroxyquinoline-4-(phenyl) sulphonamide contains three potential donor sites – (i) the quinoline ring nitrogen, (ii) the hydroxyl oxygen and (iii) sulphonamide nitrogen. The $-SO_2N$ stretching frequency appearing at 1355 cm^{-1} in the ligand 8 - hydroxyquinoline - 4 - (phenyl) sulphonamide remains almost unchanged in the respective complexes and thereby indicates the non-involvement of sulphonamide nitrogen in bonding. The two significant absorption bands due to coordinated ligand under study are ν(C=O) and ν(C-O), and these are observed in the regions, 1633-1660 cm^{-1} and 1102-1115 cm^{-1}, respectively, in the complexes. These results, which are in agreement with reported data[9] suggest the bidentate (N,O) coordination of the ligands to lanthanum in all the complexes. A broad band occurring at 3200-3400

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Table 2 – Some physical properties of the complexes

Sr.No.	Compound	Colour	Decomp. temp.(°C)	Yield (%)	Λ_M (DMF sol.) (ohm^{-1} $cm^2 mole^{-1}$)
1.	$[La(AAN)_2(HQ)]$	Yellow	230	64	9
2.	$[La(OAAT)_2(HQ)]$	Yellow	260	68	7
3.	$[La(OAAAN)_2(HQ)]$	Yellow	300	63	6
4.	$[La(AAN)_2(HQPS)]$	Yellow	160	58	10
5.	$[La(OAAT)_2(HQPS)$	White	190	55	3
6.	$[La(OAAAN)_2(HQPS)]$	White	120	57	8

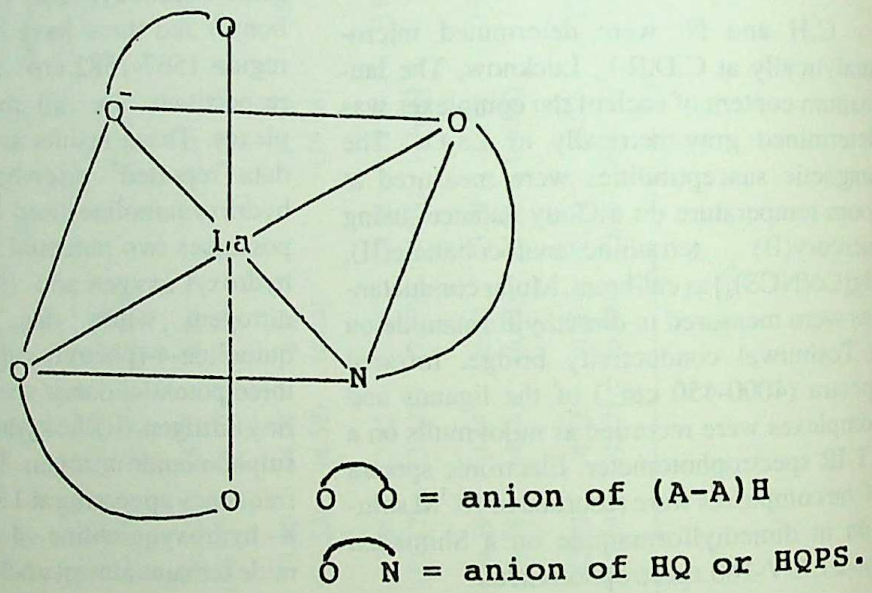

Fig. 2 – Proposed structrue of $[La(A–A)_2 (L–L)]$.

cm^{-1} in all the ligands has been assigned to ν(O-H) mode and this is found to be absent in the spectra of all the mixed-ligand complexes. This indicates that coordination of hydroxyl group in 8-hydroxyquinoline or 8-hydroxyquinoline-4-(phenyl) sulphonamide takes place after deprotonation. The overall I.R. spectral studies indicate that 8-hydroxyquinoline or 8-hydroxyquinoline-4-(phenyl) sulphonamide behave as monobasic bidentate (N,O) donors. All the complexes do not show the characteristic band(s) for coordinated water.

The observed molar conductances of all the mixed-ligand complexes in 10^{-3}M DMF solutions are in the range 3-10 ohm^{-1} cm^2

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mole^{-1}, which suggest that these mixed-ligand complexes are non- electrolytic in nature. The electronic spectra of these complexes were recorded in 10^{-3}M DMF solutions in the range 350-800 nm. All the compounds exhibit an intense band in the region 400-430 nm. This is attributed to L- M charge transfer transition[10]. All the complexes synthesized are diamagnetic.

The satisfactory analytical data and all the studies presented above suggest the formulation of these complexes as $[La(A\text{-}A)_2(L\text{-}L)]$ where (A-A)H = AANH, OAATH or OAAANH and (L-L)H = 8- hydroxyquinoline or 8-hydroxyquinoline-4-(phenyl) sulphonamide. A tri chelated octahedral structure has been proposed for the complexes as shown in Fig. 2.

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Studies on some mixed-ligand chelates of mercury (II) with o-aceto-acetotoluidide/o-acetoacetanisidide and biologically active 2-or 3-pyrazoline-5-one derivatives

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Abstract New mixed-ligand chelates of mercury(II) of the composition [Hg(Cl) (A-A) (L)], where (A-A)H = o-acetoacetotoluidide (OAATH) or o-aceto-acetanisidide (OAAANH) and L = 3-methyl-pyrazo-line-5-one (MP), 3-methyl-1-phenyl- 2-pyrazoline-5-one (MPHP), 2,3-dimethyl-4-methyl- aminomethane-sulphonate sodium monohydrate-1-phenyl-3-pyrazoline-5-one (DMMASDHP), or 4-amino-2, 3-dimethyl-1-phenyl-3-pyrazoline-5-one (ADMPHP), have been synthesized and characterised by analytical data, molar conductances, magnetic measurements, TGA and ^{1}H N.M.R. and I.R. spectral studies. The overall I.R. studies suggest that o-acetoacetotoluidide (OAATH)/o-acetoacetanisidide (OAAANH) behave as monobasic bidentate oxygen donors and the 2- or 3-pyrazoline-5-one derivatives as monodentate oxygen donors. A tetrahedral structure has been proposed for these chelates.

(**Keywords** : ^{1}HNMR/IR/magnetic studies/mixed ligand chelates/ mercury (II))

The complexing ability of acetoacetyla-rylamides, viz., o-acetoacetotoluidide and o-acetoacetanisidide are close to acetylacetone as they have the same functional groups, and are capable of keto-enol tautomerism like acetylacetone[1]. We have recently reported the synthesis and physico-chemical studies of some mixed-ligand complexes of Zn(II)[2] and mercury(II)[3] involving acetoacetanilide and different nitrogen and oxygen donors. However, there is no previous report on mixed-ligand complexes of mercury(II) with o-acetoacetotoluidide (OAATH)/o-aceto-acetanisidide (OAAANH) and 2- or 3-pyrazoline-5-one derivatives (Fig. 1), viz., 3-methyl-2-pyrazoline-5-one (MP, I), 3-methyl- 1-phenyl- 2-pyrazoline- 5-one (MPHP, II), 2,3-dimethyl-4- methylamino-methanesulphonate sodium monohydrate-1-phenyl-3- pyrazoline-5-one (ADMPHP), IV). The study of the title complexes was, therefore, undertaken and the results of these investigations are presented in this communication.

Mercury(II) chloride (B.D.H. Chemical), OAATH, OAAANH, MP and ADMPHP (Al. .ich Chemicals), MPHP (Johnson Chemical Company), DMMASPHP (obtained as a gift sample from IDPL, Hyderabad) were used as supplied. All other chemicals used were of analytical reagent grade.

The mixed-ligand complexes were prepared by mixing stochiometric quantity of the mercuric chloride (0.002 mol), OAATH/OAAANH (0.002 mol) and the ap-

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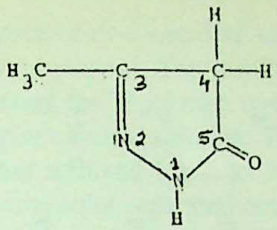
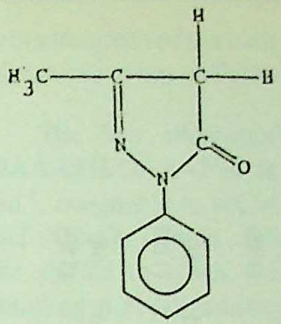
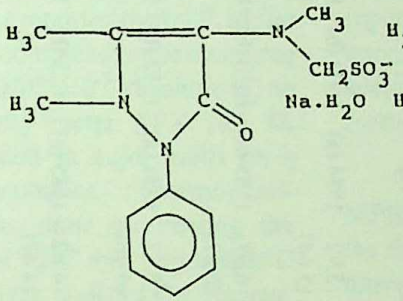


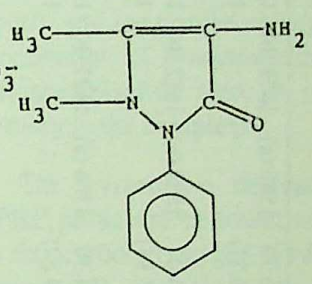
(MP)



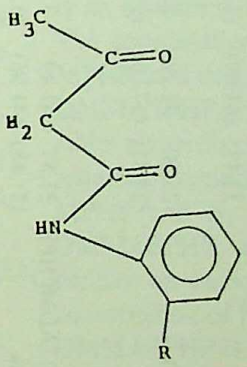
(MPHP)



(DMMASPHP)



(ADMPHP)



(acetoacetylarylamides)

Where R = CH_3, o,-acetoacetotoluidide
and R = OCH_3, o,-acetoacetanisidide.

Fig. 1 – Structure of ligands.

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Table 1 – Analytical, IR spectral data (cm^{-1}) and some physical properties of the complexes.

Sr. No.	Compound Colour	Found (Calc.) % Hg	C	H	N	Cl	ν (C=O) (Acetyl carbonyl)	ν (C=O) (Amide carbonyl)	ν (C=O) (Cyclic carbonyl)	% Yield (Decom. temp.)	(DMF sol. M (ohm^{-1} cm^2 mol^{-1})
1.	[Hg(Cl) (OAAT) (MP)] Light Pink	38.58 (38.27)	34.02 (34.34)	3.72 (3.43)	8.25 (8.01)	6.90 (6.77)	1588 (a)	1628 (b)	1550 (b) 1520*	57 (195)	7
2.	[Hg (Cl) (OAAT) (MPHP)] Light Yellow	33.72 (33.43)	41.62 (41.89)	3.27 (3.66)	6.48 (6.99)	6.07 (5.91)	1589 (a)	1612 (b)	1550 (c) 1610*	58 (110)	5
3.	[Hg (Cl) (OAAT) (DMMASPHP)] White	25.60 (25.81)	37.29) (37.06)	3.60 (3.86)	7.45 7.20	4.30 (4.57)	1586 (a)	1627 (b)	1600 (b) 1650*	68 (150)	1
4.	[Hg (Cl) (OAAT) (ADMPHP)] Yellowish Pink	31.57 (31.88)	41.49 (41.96)	3.67 (3.97)	8.68 (8.90)	5.92 (5.64)	1584 (a)	1609 (b)	1607 (c) 1665*	65 (95)	9
5.	[Hg (Cl) (OAAAN)(MP)] White	37.30 (37.14)	33.56 (33.32)	3.09 (3.33)	7.50 (7.77)	6.97 (6.57)	1585 (a)	1610 (b)	1560 (b)	56 (130)	4
6.	[Hg (Cl) (OAAAN)(MPHP)] Yellow	32.18 (32.55)	40.75 (40.90)	3.40 (3.57)	6.53 (6.81)	5.87 (5.76)	1591 (a)	1612 (b)	1552 (b)	58 (110)	6
7.	[Hg (Cl) (OAAAN) (DMMASPHP)] White	25.01 (25.29)	36.09 (36.31)	3.90 (3.78)	7.32 (7.06)	4.82 (4.47)	1585 (a)	1625 (b)	1595 (b)	67 (170)	15
8.	[Hg (Cl) (OAAAN) (ADMPHP)] Yellow	31.32 (31.09)	40.62 (40.92)	3.50 (3.87)	8.39 (8.68)	5.87 (5.50)	1585 (a)	1630 (b)	1605 (b)	64 (70)	5

*Free ν(C=O) (cyclic carbonyl) value for the respective ligand.
a = broad, medium; b = sharp, strong; c = sharp, medium.

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propriate 2- or - 3-pyrazoline-5-one derivative (0.002 mol) in 80 ml ethanol. The resulting mixture upon refluxing for 15-20 min. over a hot plate at 80°C gives a clear solution. This solution was further refluxed for 2 to 3 h. During this time some solid separated out. It was filtered by suction, washed several times with ethanol and dried in a desiccator.

Carbon, nitrogen, hydrogen were determined micro-analytically. Mercury was estimated as HgS by the reported method[6]. Molar conductances of the complexes were measured in analytical grade DMF (10^{-3} M solutions) on a digital conductivity meter APX 185. IR spectra were recorded as nujol mulls on a FT-IR spectrophotometer. Thermogravimetric analysis was done by heating the sample at the rate of 12°C min^{-1} up to 800°C on a thermal analyser at R.S.I.C., Nagpur. Magnetic susceptibilities were measured at room temperature on a Gouy balance using $Hg[Co(NCS)_4]$ as the calibrant. Decomposition temperatures of the complexes were determined using an electro-thermal apparatus having capacity to record the temperature up to 360°C.

The mixed-ligand complexes were prepared according to the following equation:

$$HgCl_2+(A-A)H+L \xrightarrow[\text{Reflux}]{\text{Ethanol}} [Hg(Cl)(A-A)(L)] + HCl$$

where (A-A) H = o-acetoacetotoluidide or o-acetoacetanisidide and L = MP, MPHP, DMMASPHP or ADMPHP. These compounds are non-hygroscopic solids. They are sparingly soluble in common organic solvents and water. The colours, decomposition temperatures and per cent yields of these complexes are given in Table 1.

The two absorption bands in IR for OAAATH/OAAANH at ~1715 and ~1655 cm^{-1}, assignable to ν(C=O) (acetyl carbonyl) and ν(C=O) (amide carbonyl), respectively, are shifted to lower wave numbers in the resulting mixed-ligand complexes, and appear at 1584-1591 cm^{-1} and 1609-1630 cm^{-1} respectively. These data are comparable to the earlier reports[7] and suggest the uninegative bidentate coordination of o-acetoacetotoluidide or o-acetoacetanisidide through the oxygens to mercury in the complexes.

The pyrazolone derivatives MP and MPHP, possess three potential donor sites : (i) the ring carbonyl oxygen (ii) and (iii) the ring nitrogens N_1 and N_2 while ADMPHP and DMMASPHP contain four common donor sites: (i) and (ii) ring nitrogens N_1 and N_2, (iii) the cyclic carbonyl oxygen and (iv) the exocyclic amino nitrogen. The sulphonate group is an additional donor site in DMMASPHP. The coordination of the ring N_1 in MP and MPHP, and ring N_1 and N_2 in ADMPHP and DMMASPHP is unlikely because of the possible zwitterion formation(s)[8] and thereby reducing the electron density on N_1 in MP and MPHP and N_1 and N_2 in ADMPHP and DMMASPHP, and increasing the electron density on carbonyl oxygen. Moreover, the coordination of N_1 in MPHP, ADMPHP and DMMASPHP is also unlikely because of the much steric demand of the phenyl ring present as substituent on these 5-pyrazolone derivatives. The ν(C=N_2) of the pyrazolone ring in MP and MPHP appearing at ~1580 cm^{-1} remains unchanged as it is merged with ν(C=O) (acetyl carbonyl) falling almost at the

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same position (1584-1591 cm^{-1}) and exhibiting one broad band. This suggests that ring N_2 is not taking part in coordination. The ν_{as}(N-H) and ν_s(N-H) in the free ADMPHP observed at 3430 and 3320 cm^{-1}, respectively, remain unperturbed in its complexes suggesting that the exocyclic amino group is inert towards coordination. The exocyclic ν(C-N) of the uncoordinated DMMASPHP observed at 1300 cm^{-1}, also remains unchanged in the spectra of its complexes. This indicates that exocyclic nitrogen in DMMASPHP is not taking part in coordination. The reason for the non-participation of the exocyclic amino nitrogen in ADMPHP/ DMMASPHP may be due to the two possible zwitterion formations (one because of cyclic amide and other due to the presence of conjugation) which are likely to make the ring carbonyl oxygen more basic as compared to the exocyclic amino nitrogen. The possibility of coordination of sulphonate group DMMASPHP was also examined. The ν(S-O) modes of the sulphonate group appear at 1095 and 1055 cm^{-1}, and these remain almost unchanged in the spectra of its complexes. This excludes any possibility of sulphonate group coordination to mercury. A comparison of the IR spectral bands of the free ligands and their complexes show that the ν(C=O) (cyclic carbonyl) observed at 1610, 1620, 1665 and 1650 cm^{-1} in uncoordinated MP, MPHP, ADMPHP and DMMASPHP, respectively, is shifted to lower wave numbers (see Table 1). This indicates the bonding of the cyclic carbonyl oxygen[9] to mercury in these complexes. The complexes do not show the characterictic band(s) for coordinated water.

^{1}H-NMR spectrum of one representative compound [Hg(Cl)(OAAT) (ADMPHP) were recorded in DMSO-d_6. It was noticed that the enolic proton appearing at 12.8 ppm in o-acetoacetotoluidide disappeared in the complexes. This suggests that enolization takes place during complexation. Rest of the protons of different viz., aromatic, CH_3, OCH_3, NH and NH_2 groups do not undergo any appreciable change after complexation. The ^{1}H-NMR data thus supports the IR results regarding the coordination sites of the ligands.

The observed molar conductance values (4-15 ohm^{-1} cm^2mole^{-1}) of all the adducts in 10^{-3}M DMF solutions indicate the non-electrolytic nature of these complexes. All the mixed-ligand complexes synthesized are diamagnetic.

The thermogravimetric curve of one of the representative compounds, [Hg(Cl) (OAAAN) (DMMASPHP)], was recorded in the temperature range 40-775°C. This shows that the compound is stable up to ~170°C and starts decomposing above this temperature and the process completes around 400°C. The weight loss observed is equivalent to the elimination of one unit each of o-acetoacetanisidide, DMMASPHP and Cl (theoretical weight loss = 74.7% and observed weight loss = 75%).

The analytical data (Table 1) and all the results discussed above suggest that the mixed-ligand complexes may be formulated as [Hg(Cl) (A-A) (L)] (where (A-A)H = o-acetoacetotoluidide or o- acetoacetanisidide, and L = MP, MPHP, DMMASPHP or ADMPHP). A tetrahedral structure has been tentatively proposed for these complexes.

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Organochlorine pesticide residues in milk of two distinct agro-geoclimatic regions of Uttar Pradesh, India

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Abstract On account of their extensive and unregulated use and their lipophilic nature, OCP residues or their isomers and/or metabolites have been detected in almost every components of the environment. Preliminary studies on milk samples from two regions of Uttar Pradesh have revealed the presence of p,p' - DDD, p,p' - DDE, and HCH - isomers in these. The level of residues was higher in the samples analysed from Lucknow markets.

(**Keywords** : organochlorine pesticides/HCH/ DDT/ milk/geoclimatic conditions)

Milk, an important part of our diet has been found contaminated with organochlorine pesticide (OCP) residues, such as hexachlorocyclohexane (HCH) and dichlorodiphenyl trichloroethane (DDT). Reports are also available of their presence in other food items.

District Pithoragarh, rich in fauna and flora and Lucknow, capital of Uttar Pradesh was selected for this work.

Analytical standards for OCP were obtained from USEPA Pesticides and Industrial Repository (MD-8), Research Triangle Park, NC, USA. All solvents and chemicals used in extraction and clean-up process were of A.R. Grade and distilled in glass-still prior to use. Florosil (Fluka, A.G.), silica gel (Glindia Ltd.), activated charcoal (E. Mark India Ltd.) and Sodium Sulphate anhydrous (Sarabhai Chemical, Bombay) used in this experiment were of high purity. The purity of the test compounds was checked by thin layer chromatography (TLC) on silica gel coated glass plates using n-Hexane as mobile phase and subsequently Gas Liquid Chromatography.

A total of 30 samples (each in triplicate), belonging to 15 from District Pithoragarh (Didihat, Gagolihat, Lohaghat, Pithoragarh and Thal) and 15 from Lucknow markets (Alambagh, Chowk, Daliganj, Kaiserbagh and Nisatganj), were collected and analysed using 50 ml for each[1]. Fat (after extraction), was separated by acetonitrile, partitioning (saturated with a n-Hexane), and pesticide residues were re-extracted in n-Hexane and passed through florisil column. The clean-up and GLC analysis were carriedout as described elsewhere[2,3].

The results obtained from the monitoring survey of District Pithoragarh (Himalayan Hills) and Lucknow (U.P. Plain), are comparable and presented in Table 1.

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Table 1 – Residues levels of organochlorine pesticides in milk, collected from District Lucknow and District Pithoragarh of Uttar Pradesh, India (1990).

Residues (ppm)	Location	
	Lucknow	Pithoragarh
p,p' -DDD	0.7702* (0.4400-0.9010)**	0.0315 (0.0012-0.6741)
p,p' -DDE	0.1001 (0.0141-0.1803)	0.0008 (0.0003-0.0016)
DDT (Total)+	0.8711 (0.6203-0.9720)	0.0323 (0.0021-0.0757)
Alpha-HCH	0.0194 (0.0040-0.0410)	0.0028 (0.0009-0.0087)
Beta-HCH	0.456 (0.0251-0.0703)	0.0032 (0.0011-0.0097)
Gamma-HCH	0.0101 (0.0081-0.0133)	0.0009 (0.0001-0.0017)
HCH (Total)++	0.0750 (0.0373-0.1111)	0.0069 (0.0021-0.0194)

* Indicates mean of five values, each in triplicate.
** Indicates values in range.
+ DDT (Total) : Sum of its metabolites and isomers.
++ HCH (Total) : sum of alpha-, beta-, and gamma-isomers.

Residues of HCH, p,p' -DDD, p,p' - DDE were found in all samples. Total DDT was highest in samples from Alambagh (0.9720 ppm) followed by Chowk (0.9704 ppm), Nisatganj (0.8991 ppm), Kaiserbagh (0.8941 ppm) and Daliganj (0.6203 ppm) markets of Lucknow. Samples analysed from district Pithoragarh collected from Didihat had maximum (0.0757 ppm), residues of total DDT followed by Gagolihat (0.0632 ppm), Lohaghat (0.0105 ppm), Thal (0.0102 ppm) and Pithoragarh (0.0021 ppm). Total HCH was found highest in milk from Daliganj (0.1111 ppm) followed by Kaiserbagh (0.1003 ppm), Chowk (0.0636 ppm), Alambagh (0.0631 ppm) and Nisatganj (0.0373 ppm). While in district Pithoragarh it was highest from Didihat (0.0194 ppm) followed by Lohaghat (0.0052 ppm), Gagolihat (0.0047 ppm), Thal (0.0034 ppm) and Pithoragarh (0.0021 ppm).

p,p' -DDT is known to undergo metabolic conversion and dehydrochlorination[4]. The presence of p,p' -DDD and p,p' -DDE encountered in this study, but p,p' -DDT was not

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detected itself in any sample. HCH was found as alpha, beta and gamma-isomers in every analysis. The level of DDT (total) and HCH (total) was higher in samples from Lucknow market.

The main route of human exposure to many oranochlorine pesticides is through food of animal origin, where milk is the most important product. Milk is considered as one of the convenient indicators for measuring the extent of persistent residues that can be originated from contaminated animal feed and extensive use in the control of ectoparasites of livestock. The hazardous presence of these non-degradable pesticides is a matter of global concern, as pharmacological studies had demonstrated that small excess of these can cause serious disorders. Furthermore in tropical climate, as Lucknow, the biological transformation is relatively rapid due to heat, light, humidity and microbial activity. So considering the impact of pesticide residues on human health, it is therefore imperative to take into account climatic, socio-economic, ethnic and health background of people.

The study indicates that there is need for monitoring of these pesticides in varied agro-climatic conditions.

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Precise Range and Rangerate Equipment (PRARE)

Received April 8, 1997.

Abstract The Precise Range and Rangerate Equipment (PRARE) is an universal space based microwave tracking system, which was launched for the first time on ERS-1, satellite in 1991 by ESA. PRARE, presently on ERS-2 satellite, is providing its host satellite with highly accurate tracking information by two-way rangerate measurements , supplemented by ionospheric corrections and metrological data. These data are used for precise orbit determination, for absolute positioning of remote ground stations as well as for precise baseline determination with interstation distances of up to about 1000 km, in length. The PRARE system consists of a small additional package in the satellite, a number of low cost ground stations operating as coherent regenerative transponders and of a master ground station for system command and data transfer. Compressed tracking data from the spaceborne transreceiver together with corrective data transmitted from the remote stations is stored in the onboard memory of the system. Within the next 12 h they are transferred to the master station which is linked to the analysis centre for archiving and processing the data. This communication describes the PRARE station at Bangalore, data flow and interface definitions, measurement accuracies and shows the capability of this tracking system to operate autonomously and almost unattended.

(**Keywords** : space based microwave tracking system/range rate measurements)

Introduction : PRARE is an autonomous, spaceborne, twoway, dual frequency microwave tracking system with its own telemetry, telecommand, data storage, timing and data transmission capability. The PRARE system was developed and manufactured under the grant of German ministry of research and technology (BMFT) by the following institutions:

- Institut fuer Navigation (INS), Stuttgart (system design and spacecraft operation)
- Geo Forschungs Zentrum (GFZ), Potsdam (master and calibration station operation, data decoding, pre and post processing, tracking network coordination, generation of prediction elements)
- Deutsche Gesellschaft fuer Luft-und Raumfahrt (DLR), Oberfpfaffenhofen (housing of the master station at the D-PAF)
- Dornier, GmbH, Munich (industrial contractor for space segment)
- TIME TECH GmbH, Stuttgart (system integration, test and calibration)
- Deutsche Agentur fuer Raumfahrtangelegeiten (DARA), Bonn (financing)

System Description: PRARE system as shown in Fig. 1 is made up of three basic components:

* The universally applicable space segment with minimum interface to its host satellite.
* A number of small low cost tracking ground stations operating almost unmanned which can easily be transported and installed universally. The G/S are small in size highly mobile and have a low power consumption.
* The control ground station, differs only from the tracking station in that it is additionally capable of data communication at a higher bit rate, clock synchronisation and data storage. This station can operate in the same way as the tracking stations above but

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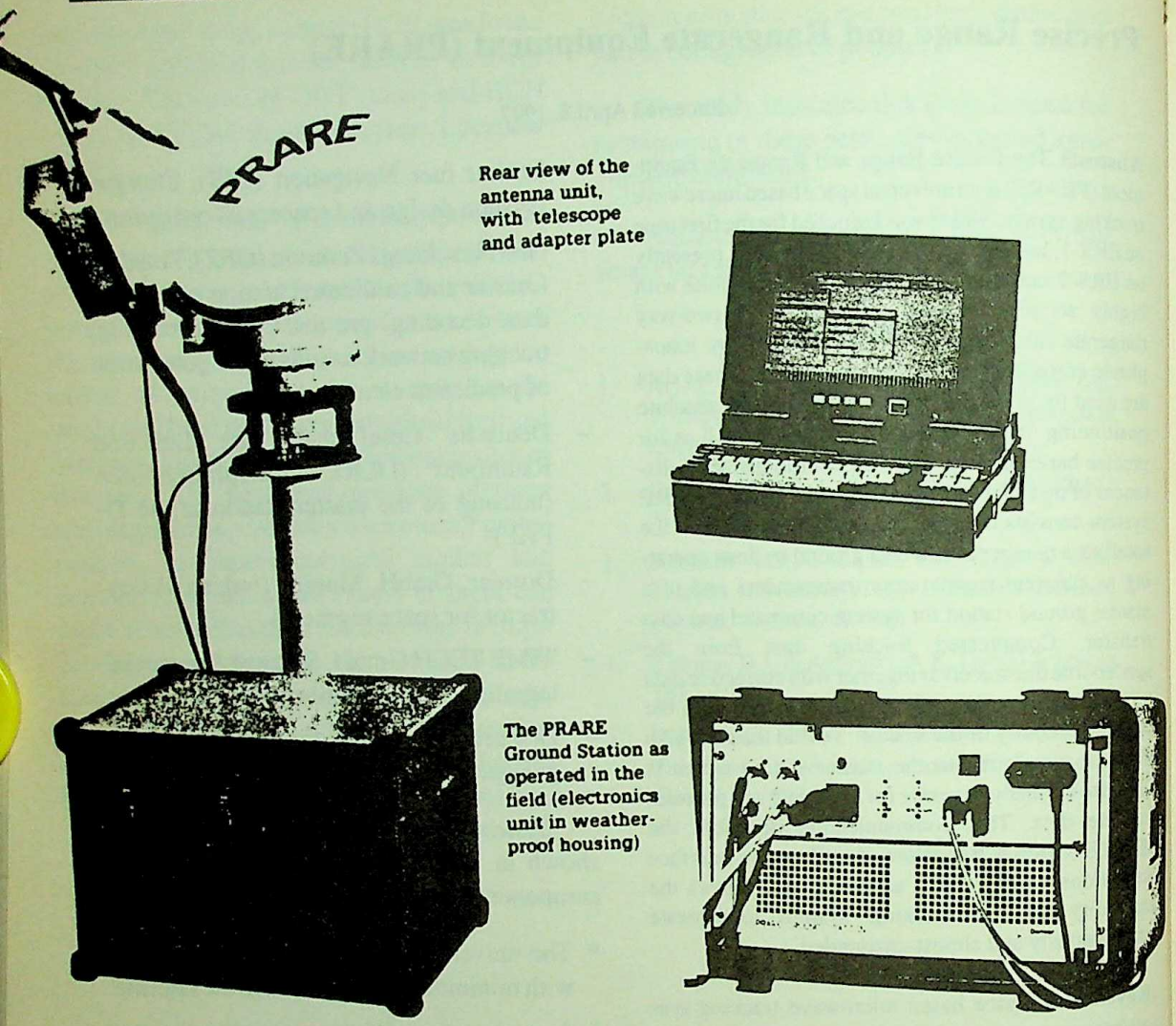

Fig. 1 – PRARE ground station.

its function is dedicated to the transfer of control commands and the reception of the complete measurement unformation and will be directly linked to an archiving, processing and distribution centre.

The PRARE tracking principle is explained in Fig. 2. The space segment emits to the earth two pseudo random noise (PN) coded microwave signals in X band (8.5 GHz) and S band (2.25 GHz) frequencies which allow the system to operate in all weather conditions. Nevertheless the measurements are only slightly affected by atmospheric refration. The ground station receives the two simultaneously emitted signals with a slight time difference and determining the time lag as a measure for

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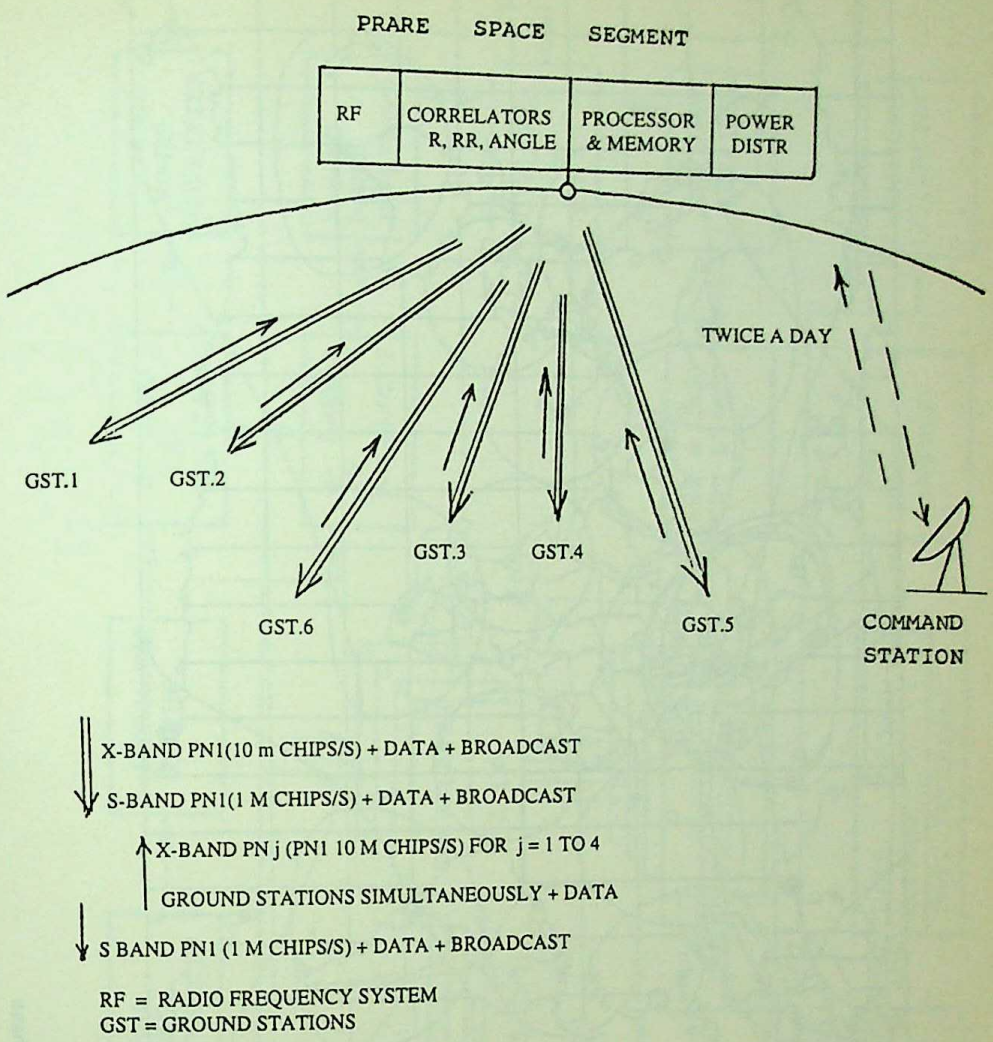

Fig. 2 – PRARE tracking system principle.

the ionospheric refration in the atmosphere passed through. The received signals are demodulated and a coherent regenerated copy of the PN sequence at X band (7.2 GHz) is retransmitted to the space segment where the twoway travel time (range) and the twoway doppler (rangerate) measurements are carried out. The retransmitted PN sequence from the ground station to the satellite will be one of four possible converted orthogonal series with respect to the received one which enables twoway measurements for up to four individual stations simultaneously (code multiplexing). Both measurement links, space to

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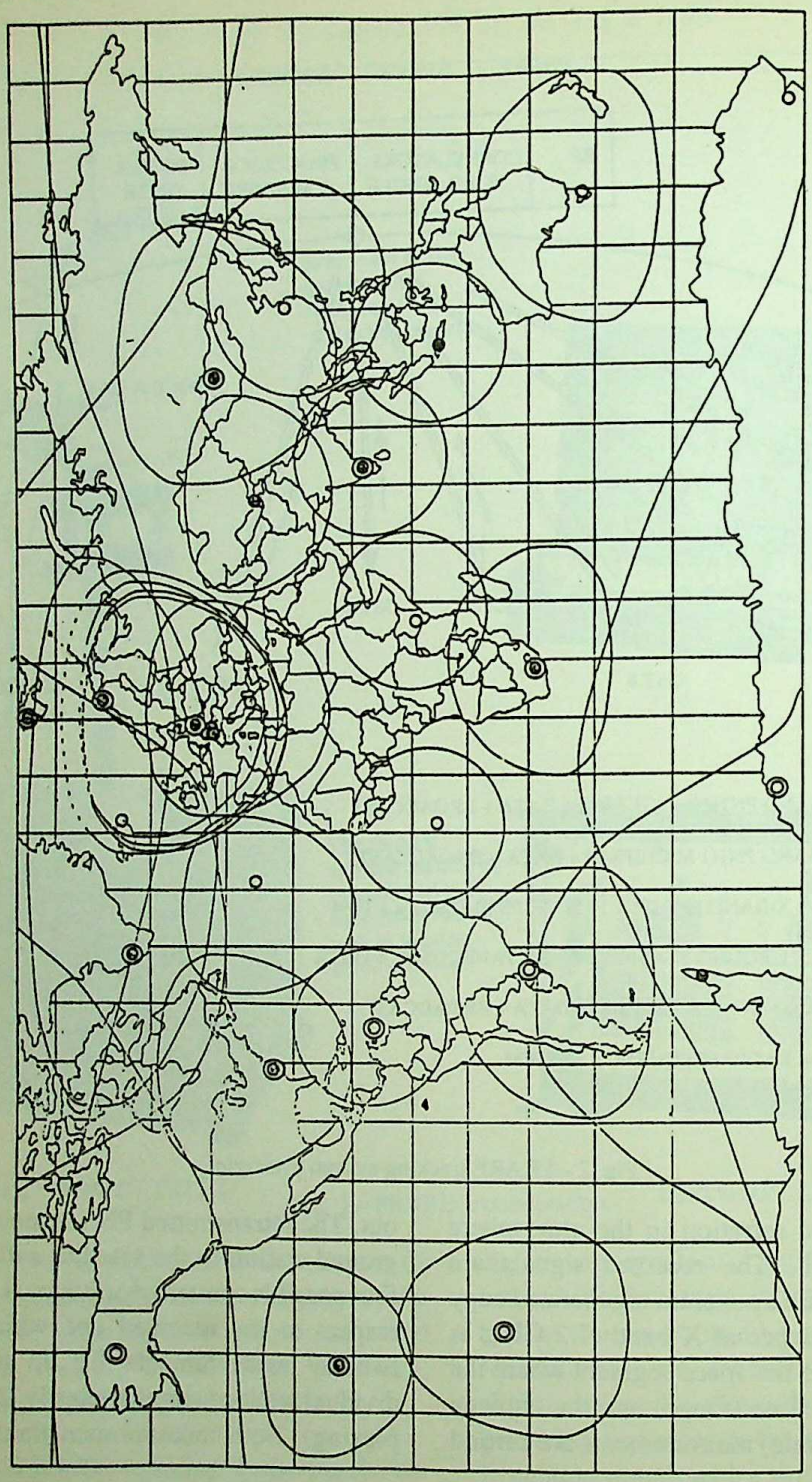

◎ MEX Stations
● Operational Stations
○ Plannig or installation phase

Fig. 3 – PRARE ground station network

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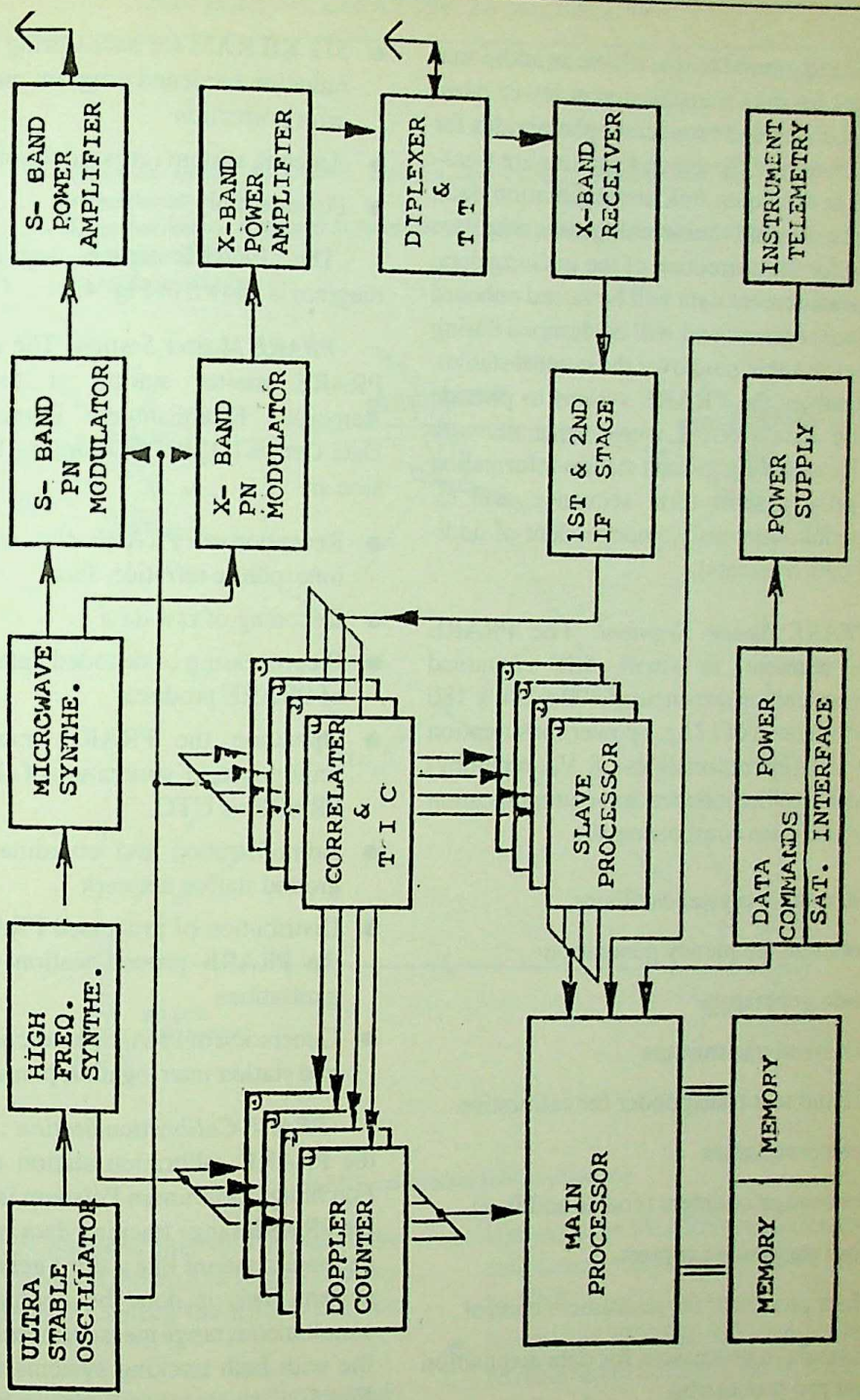

Fig. 4 – PRARE space segment : synthesizer, radio frequency system and data processing units.

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ground and ground to space have an additional capacity for data transmission at lower rates. Control codes and broadcast ephemerides for the operation of the ground stations are transmitted in the down link and calibration data, ionospheric and meteorological data are needed for the correction of the tracking data. The measurement data will be stored onboard the space segment and will be dumped during the next suitable pass over the control station. This enables the PRARE system to provide tracking data from a world wide network (Fig. 3), including ground station information after only a short term sequence, and to, operate autonomously (independent of additional data transfers).

PRARE Space Segment: The PRARE space segment is small self contained hardware unit of dimensions 400 x 240 x 180 mm with a mass of 17 kg, a power consumption of 39 VA (operational) and 8 VA (standby) and host satellite independent communication links. The main components are

- Ultrastable crystal oscillator
- Coherent frequency generation
- Code generators
- S/X band transmitters
- X band text transponder for calibration
- Four correlators
- Four range counters (coarse and fine)
- Four rangerate counters
- Main processor for instrument control
- Four slave processors for data acquisition and pre-processing
- 512 KB RAM for data storing and 64 KB radiation hardened program memory with error correction
- Antenna system (crossed dipoles)
- Power supply

The PRARE space segment block diagram is shown in Fig. 4.

PRARE Master Station: The tasks of the PRARE master station at the German Aerospace Establishment Remote sensing Data Centre (DLR/DFD) during ERS-2 mission are

- Reception of PRARE raw tracking and ionospheric refration data.
- Decoding of raw data
- Preprocessing of decoded data generation of PRARE products
- Operation the PRARE master station timing system, generation of clock models PRARE vs UTC.
- Administration and coordination of the ground station network
- Distribution of processed PRARE data to the PRARE ground station owning organisations
- Generation of PRARE prediction elements and station interrogation plans

PRARE Calibration Station : The task of the PRARE calibration station at the GEO Forchungs Zentrum in Potsdam is to compare the PRARE range tracking data with an international standard like a third generation laser system. This is done by comparing quasi-simultaneous range measurements to the satellite with both tracking systems as shown in Fig. 5

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$\vec{d}_s$ - difference vector at satellite between the PRARE antenna and the Laser retroreflector
$\vec{d}_g$ - difference vector at ground between the PRARE transponder and Laser system
$l(t)$ - Laser observation
$p(t)$ - PRARE observation

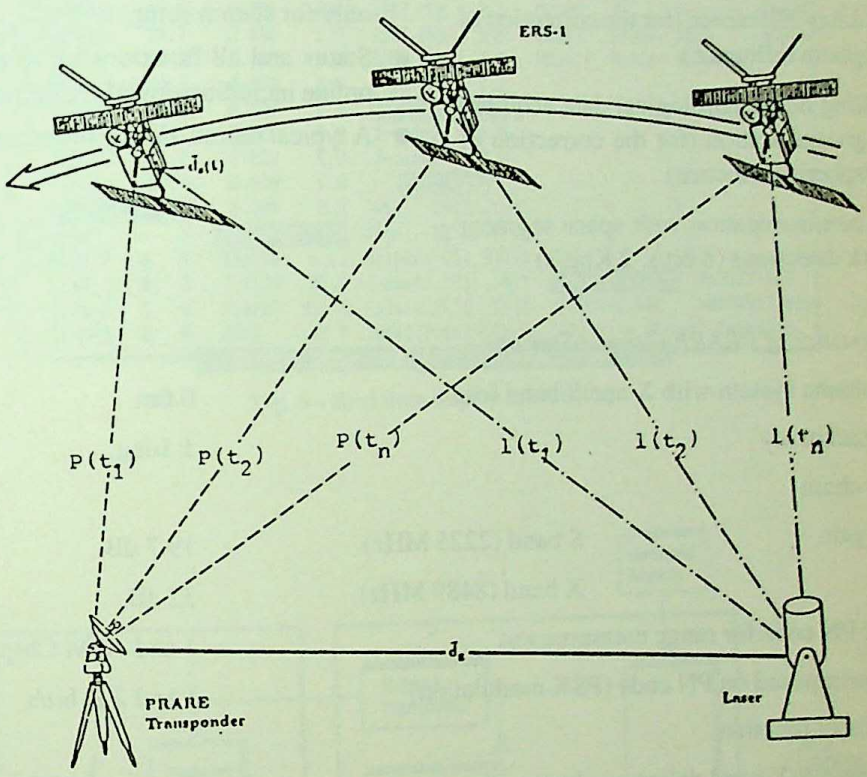

Fig. 5 – PRARE calibration station principle.

PRARE Command Station: The task of the command station at the Institut fuer navigation in Stuttgart (INS) during the ERS-2 mission are

- Inflight system monitoring and commanding
- Updating the PRARE prediction elements and station interrogation plans generated by GFZ
- Initiate the PRARE data dump which can be received in Stuttgart, Oberpfaffenhofen and Potsdam

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PRARE Ground Stations :

Functions :

- Regenerative, coherent X band transponder for precise range and rangerate measurements
- S band receiver and measurement of S/X band delay difference (for the correction of ionosphere influence)
- Handling of meteorological data acquired near ground station (for the correction of tropospheric influence)
- Data communication with space segment in both directions (8 bit/s, 2 Kbit/s)

Features

- Highly mobile, to be hand carried in separate units
- Modular design, no maintenance necessary
- Automatic operation, personnel required only for station setup
- Status and all functions to be monitored online including downlink/uplink data
- A typical online display is shown in Fig. 6

Characteristics of PRARE Ground Stations.

Offest antenna system with X and S band feed		0.6m
Tracking accuracy		± 1deg.
Receiver chain		
Antenna gain	S band (2225 MHz)	19.7 dB
	X band (8489 MHz)	32 dB
S/X band PN code for range measurement		1 and 10 M Chip/s
Data superimposed on PN code (PSK modulation)		1 and 2 K bit/s
Measurement function		
Difference of S/X band delay, resolution		30 ps
Internal station delay		30 ps
Transmit chain		
Antenna gain	X band (7225 MHz)	30.8 dB
Transmitter power		5 W
PN code (carrier and PN code regenerate)		10 M Chip/s
Data super imposed in PN code (PSK modulation)		1 and 2 K bit/s

The block diagram of PRARE ground station is shown in Fig. 7.

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```
PRARE Monitor & Test Computer Operational Mode (V4.20)
1993/01/28 11:12:59   Message received: Meteo. Stat. Data 1993/01/28 11:12:31

GS-Temp   [°C]   X/X[m]  X/S[m]   GS-Frequ  [Hz]                GS-Status
X-DLL     54.6   0.000    0.0    X-PLL  9646589   Set Up  Malt   Warm Up  Calib
X-PLL     47.3   0.000    0.0    X-DLL  9999513   Acquis  Orbit  Sat Rec  -----
S-DLL     54.6   0.000    0.0    S-PLL 10700002   HPA     Modul  TT       X-DLL
S-PLL     45.3   0.000    0.0    S-DLL   999902   X-PLL   S-DLL  S-PLL    Fan
X-Syn.I   42.4   0.000    0.0   GS-Volt.   [V]                GS-Errors
X-Syn.II  37.7   0.000    0.0   7200 MHz   5.3   VXCO    I/O    Temp     TIC
X-Conv.   41.9   0.000    0.0   1263 MHz   0.1   Meteo   TT     -------  CodeX
S-Syn.    38.7   0.000    0.0   1205 MHz   3.0   CodeS   Level  SSyn     XSynI
S-Conv.   40.4   0.000    0.0   2054 MHz   3.6   XSynII  Orbit  Antenna  -----
Frontend  24.3   0.000    0.0    172 MHz   3.7
Cable     25.0   0.000    0.0   AGC-Values [V]
TIC1      45.7   0.000    0.0   X-coded    0.0
TIC2      43.2   0.000    0.0   S-coded    0.0
TIC3      39.5   0.000    0.0      Next Pass
Count     X   S   0.000    0.0  Date    1993/01/28
HRD       0   0  Meteo Station  Time    12:05:40.7
LRD-0     0   0  Status    o.k.  Azimuth [°] 358.3
LRD-1     0   0  T [°C]    25.2  Elevat. [°]   0.9  Current Files:  PASS17.021
LRD-2     0   0  P[hPa]   951.4  Culmin. [°]  13.7  STATUS17.DAT    HRDATA17.021
LRD-3     0   0  H[%]      33.7  Durat.[sec] 681.6  <F1> Help <Enter> Continue
Current space on disk  73 MB (366 passes)
```

Fig. 6 – Real time display monitoring.

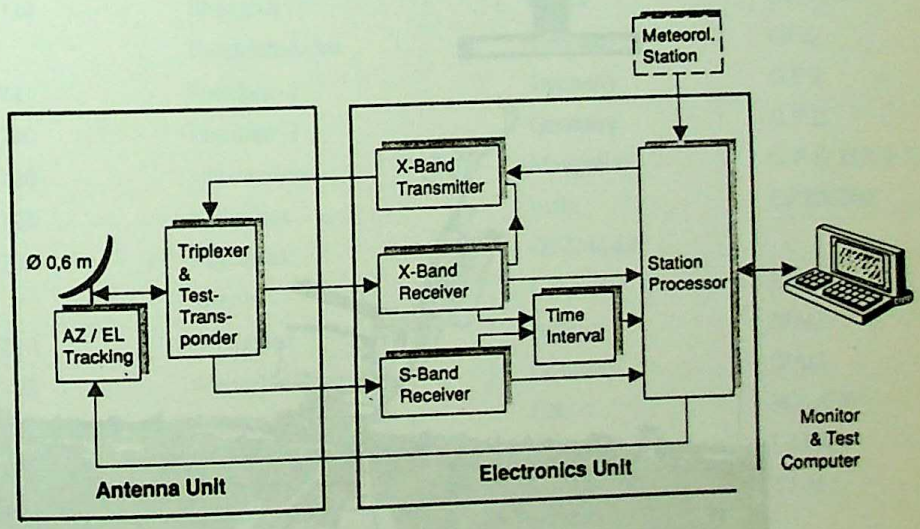

Fig. 7 – Block diagram of PRARE ground station.

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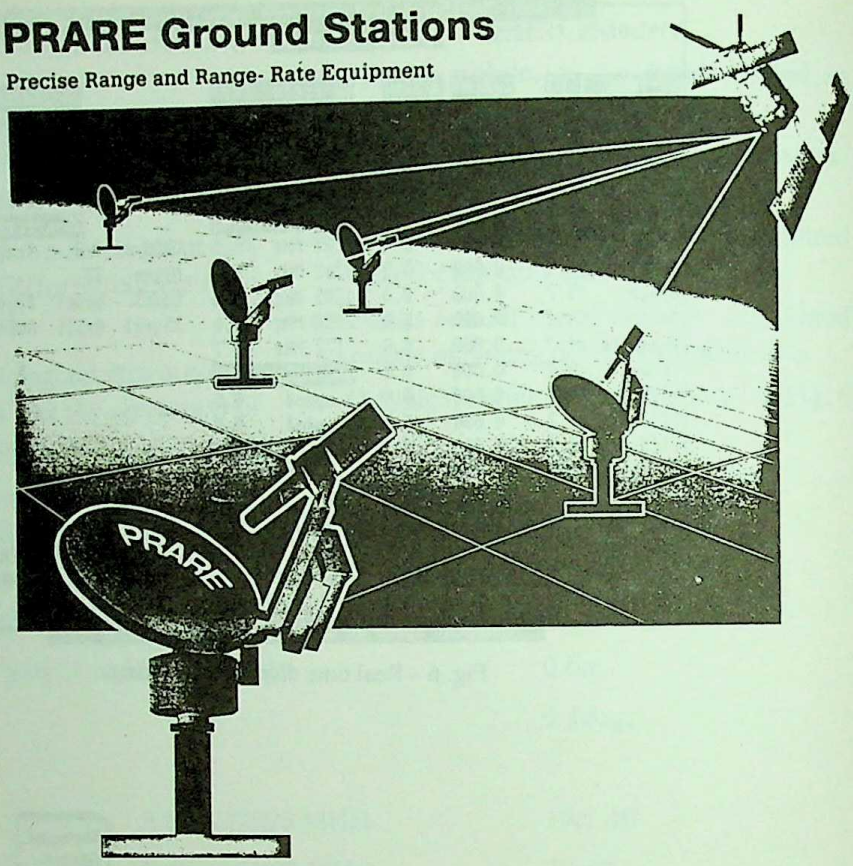

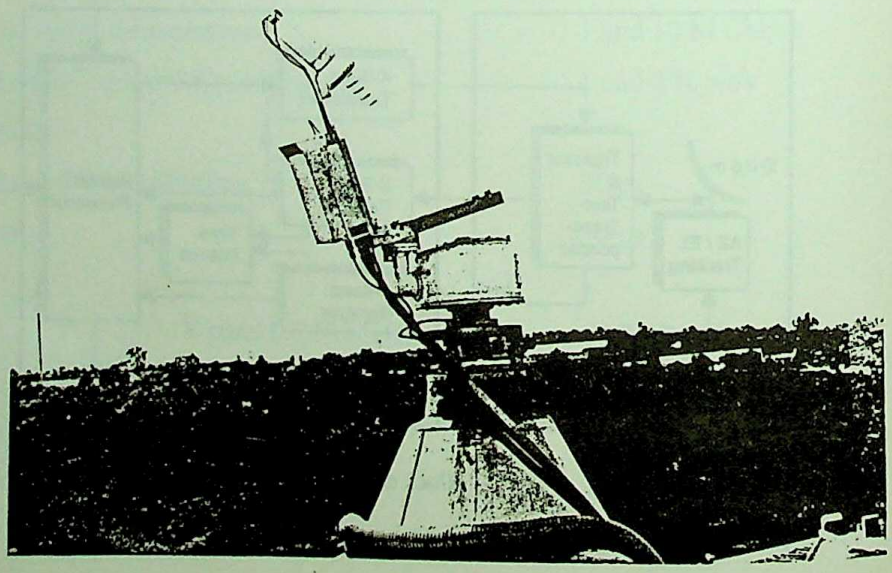

Fig. 8 – Bangalore PRARE station.

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PRARE Ground Station Network

Sl No.	COSPAS No.	Station location	Country	Owner agency
1	7730	Potsdam	Germay	GFZ
2	736	Oberpfaffenhofen -1	Germany	GFZ
3	7701	Oberpfaffenhofen -2	Germany	GFZ
4	7757	Tokyo	Japan	NIPR
5	7754	Neumayeu	Antract	A W I
6	7706	Narsarsuag	Greenland	U C
7	7756	Matera -1	Italy	A S I
8	7704	Matera -2	Italy	A S I
9	7755	Greenbelt -1	USA	CSR/GTRC
10	7724	Kokee park	USA	CSR
11	7709	Tahiti	France	CSR
12	7722	Greenbelt -0	USA	DUT/GSFC
13	7728	Nyalesund	Spitsbg	S K
14	7702	Tromsoe	Norway	S K
15	7716	Maracaibo	Venezue	S K/DGFI
16	7721	Kitab	Usbekistan	GFZ/AOK
17	7714	Hartebeessthock	S Africa	GFZ/SAO
18	7734	Shanghai	China	GFZ/SAO
19		Freidrichshafen	Germany	GFZ/
20	7741	Potsdam -2	Germany	G F Z
21	7740	Potsdam -1	Germany	G F Z
22	7720	Ulaanbaatar	Mangolia	G F Z/ ISRO
23	7725	Bangalore	India	GFZ/ISRO
24	7715	Argentina	GFZ/AOLP	
25		Munich	Germany	DGFI/S K
26	7710	O'Higgins	Antract	IFAG
27	7703	Wettzell	Germany	IFAG
28	7717	Ascension	UK	POL/CW
29	7718	Bogor	Indonesia	LAPAN
30	7700	Stuttgart	Germany	T I M

The PRARE network is shown Fig. 3.

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Applications : Primarily PRARE is used to support the radar altimeter measurements and to extend the mission goal to geodetic and geodynamic purposes, mainly as below:

Orbit determination for ERS-2(985 km polar sunsynchronous) together with laser tracking

* To complement the global laser tracking network by an alweather tracking system for better data coverage and improved long arc orbit determination
* To obtain high precision orbit determination on a regional scale by concentrating the tracking system in specific areas

Investigation of ionospheric refraction influences and determination of travel time corrections.

Collection of world wide meteorological data as input to ionospheric refration models for PRARE and other sensors

Baseline determination between PRARE ground stations

*For geodetic network control

*For monitoring of crustal movements

PRARE Accuracies: The PRARE measurement accuracy is governed mainly by the hardware limitations and the refraction model uncertainties.

On the basis of the hardware components realised sofar the measurement precision (rms) is estimated to be

+/- 1.7 cm for X band ranging

+/- 30 cm for S band ranging

+/- 0.1 mm/s for X band doppler

The given value refer to 1 measurement/s for ranging and to an integration interval of 30 s for the doppler measurement, both at the elevation of 90 deg. assuming oneway distances and velocities respectively.

Maximum bias values for the range measurement due to the phase locked loop dynamics is estimated to be

< 1 cm for X band

< 3 cm for S band

Tracking error estimation for range measurement is

Tropospheric error	$\delta R_T = 2 - 7$ cm
Ionospheric error	$\delta R_I = 1 - 2$ cm
Thermal noise and calibration error	$\delta R_c = 2 - 3$ cm
Antenna phase uncertainity	$\delta R_A = 1$ cm

$$R\,S\,S = \sqrt{\delta R_T^2 + \delta R_I^2 + \delta R_C^2 + \delta R_A^2}$$

$$3 \text{ cm} < R\,S\,S < 7 \text{ cm}$$

Conclusion : Bangalore PRARE is providing support for the last two years (initially for Russian satellite METEOR 3/7 and currently supporting ERS-2) along with a co-located P-code GPS receiver (Turbo Rogue SNR 8100). There is a proposal for establishing a third generation satellite laser ranging (SLR) system at Bangalore which will elevate Bangalore as a primary centre in the international I G S network and Bangalore will also join the calibration stations for the PRARE network.

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Some results of Bangalore PRARE station

STATION: 77259001 (306.9 sec)

Name: BangaloreX: 1344099.182, Y: 6068610.949 Z: 1429283.026 Breite: 13.0342334

Laenge: 77.5115129 Hoehe: 834.130

Pass	Beob	Ausr	Start Datum/Zeit	Dauer [sec]	Bed [%]	AOD [deg]	(Az)	Culm. [deg]	(Az)	LOD [deg]	(Az)
1	592	8	9-OCT-1995 04:26:16.423	593.0	99.8	7.8	(51.8)	18.3	(99.7)	2.2	(157.4)
2	605	8	9-OCT-1995 06:04:40.423	653.0	92.6	7.8	(346.3)	28.7	(285.2)	3.4	(218.7)
3	811	8	9-OCT-1995 17:05:03.422	813.0	99.8	3.9	(166.8)	88.4	(75.0)	1.5	(348.4)
4	552	8	10-OCT-1995 18:15:39.422	553.0	99.8	6.1	(218.4)	13.9	(260.6)	2.4	(311.7)
5	591	8	11-OCT-1995 05:04:01.422	593.0	99.7	20.9	(34.0)	50.3	(101.6)	2.8	(180.4)
6	591	8	14-OCT-1995 05:09:43.422	593.0	99.7	22.3	(28.7)	59.3	(102.0)	2.9	(183.7)
7	473	8	14-OCT-1995 06:47:53.422	473.0	100.0	2.7	(324.6)	8.2	(288.2)	2.7	(251.6)
8	653	8	14-OCT-1995 16:09:39.422	653.0	100.0	3.7	(129.6)	18.8	(73.9)	3.0	(17.3)
9	707	8	14-OCT-1995 17:48:15.422	709.0	99.7	4.2	(194.1)	28.2	(259.7)	3.5	(326.2)
10	497	8	15-OCT-1995 04:39:01.423	497.0	100.0	16.5	(58.4)	24.9	(100.1)	4.5	(162.3)
11	669	8	15-OCT-1995 06:15:29.422	669.0	100.0	4.3	(343.6)	21.3	(286.0)	2.8	(225.8)
12	353	8	15-OCT-1995 15:41:25.422	353.0	100.0	4.3	(96.2)	6.8	(71.3)	3.1	(41.3)
13	771	8	15-OCT-1995 17:16:34.422	773.0	99.7	4.5	(173.9)	67.7	(258.4)	3.3	(342.8)

A Raw RMS [cm]	Bias 1 [cm]	Sigma	Bias 2 [msec]	Sigma	Poly RMS [cm]	NP	3si	Ite	ges	NP RMS [cm]
50.1	43.5	2.2	0.036	0.006	3.190	39	20	6	0	0.504
25.2	-0.7	1.0	0.036	0.002	2.679	41	4	2	0	0.637
47.6	26.4	1.8	-0.046	0.003	2.443	52	68	8	4	0.419
18.3	-9.4	0.8	-0.002	0.003	2.108	37	23	8	0	0.435
40.4	27.6	1.9	0.037	0.004	2.245	39	8	3	0	0.424
57.9	23.5	2.7	0.082	0.005	1.800	39	2	2	0	0.314
78.5	75.8	3.7	0.017	0.016	4.317	32	2	2	0	1.039
55.5	1.2	2.2	-0.138	0.006	3.520	43	9	4	0	0.660
79.7	34.8	3.3	-0.190	0.008	1.780	42	23	6	83	0.308
29.5	0.6	1.6	-0.072	0.004	2.064	33	8	3	0	0.462
60.3	34.2	2.4	-0.136	0.006	3.087	42	7	4	34	0.752
22.7	-19.4	1.2	-0.022	0.007	4.200	23	0	1	0	1.050
63.0	15.4	2.3	-0.111	0.004	2.229	52	6	4	0	0.335

kart. Koord. gelesen:	1344099.182	6068610.949	1429283.026
kart. Koord. geloest:	1344099.033	6068610.589	1429283.320
Differenz :	0.149	0.360	-0.294
geog. Koord. gelesen:	13.0342334	77.5115129	834.130
geog. Koord. geloest:	13.0342368	77.5115152	833.623
Differenz :	-0.0000034	-0.0000023	0.507

Korrelationen (X/Y),(X/Z),(Y/Z):	0.220	0.003	0.302
Sigma:	0.009	0.014	0.009

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Interne Id 19 (Bangalo)

P	Start	Dauer [sec]	Bed [%]	F0 [%]	F1	F2	F3	F4	F5	AGC0 [V]	AGC1 [V]	Temp [C]	A#H	#R	Ion-Bedeckung
1	9-OCT-1995 04:25:51	636	100.0	99.5	0	0	1	2	0	3.11	4.92	21.8	11	10	TTTTTTTTTTF
2	9-OCT-1995 06:03:42	748	93.9	98.2	0	0	3	10	0	2.87	3.94	21.8	11	11	TTTTTTTTTTF
3	9-OCT-1995 15:30:46	300	69.1	67.8	0	0	2	65	0	3.15	4.80	22.8	2	2	FT
4	9-OCT-1995 17:04:59	824	100.0	99.3	0	0	2	4	0	2.99	5.00	22.8	14	14	TTTTTTTTTTTTTT
5	9-OCT-1995 18:49:13	276	100.0	24.2	0	0206		2	2	3.19	5.28	22.8			
6	10-OCT-1995 18:14:38	634	100.0	98.1	0	0	1	11	0	3.11	5.00	22.9	10	10	TTTTTTTTTT
7	11-OCT-1995 05:03:15	651	100.0	98.3	0	0	3	8	0	2.87	3.42	21.8	11	10	TTTTTTTTTTF
8	14-OCT-1995 05:08:41	686	96.8	98.5	0	0	2	7	1	2.99	5.00	21.8	10	10	TTTTTTTTTT
9	14-OCT-1995 06:47:43	501	100.0	98.2	0	0	1	8	0	2.94	4.60	21.8	9	8	TTTTTTTTF
10	14-OCT-1995 16:09:28	686	100.0	99.1	0	0	1	5	0	3.03	5.65	22.9	12	12	TTTTTTTTTTTTF
11	14-OCT-1995 17:48:04	748	97.3	98.6	0	0	2	8	0	2.99	5.46	22.9	12	12	TTTTTTTTTTTT
12	15-OCT-1995 04:38:15	578	100.0	95.3	0	0	23	1	3	3.07	4.96	21.8	T 9	9	TTTTTTTTT
13	15-OCT-1995 06:15:21	699	100.0	97.9	0	0	0	14	1	2.87	4.68	21.9	12	12	TTTTTTTTTTTT
14	15-OCT-1995 15:40:32	471	87.5	98.1	0	0	0	8	0	3.03	5.50	22.8	6	6	TTTTTT
15	15-OCT-1995 17:16:22	794	99.9	99.1	0	0	2	5	0	2.96	5.46	22.9	13	13	TTTTTTTTTTTTT
16	16-OCT-1995 04:06:09	541	99.8	99.3	0	0	1	3	0	2.94	4.53	21.8	9	9	TTTTTTTTT
17	16-OCT-1995 05:44:40	731	96.9	98.2	0	0	2	11	0	2.99	5.00	21.7	11	11	TTTTTTTTTTT

Station 19: 10256 Beobachtungen in 17 Passagen

XSmin [m]	XSmax [m]	XXmin [m]	XXmax [m]	Pmin [HPa]	Pmax [HPa]	Tmin [C]	Tmax [C]	Hmin [%]	Hmax [%]	K	TT [m]	Output/Kommentar
13.7	16.8	135.105	135.180	912.9	912.9	21.3	21.7	79.4	80.1	1	62.501	D1995282.160
13.0	16.5	135.110	135.175	911.2	911.5	22.7	23.5	69.5	69.9	0	64.216	D1995282.218
10.5	11.2	135.035	135.145	910.9	910.9	21.6	21.6	73.0	73.0	2	60.370	D1995282.558
9.8	205.0	134.400	135.190	911.7	911.7	20.3	20.6	71.1	73.0	2	60.370	D1995282.615? X/S ! zu wenig XS Data
9.6	11.8	135.155	135.195	908.9	909.0	20.0	20.0	88.0	88.0	2	60.370	D1995283.657
11.6	16.0	135.000	135.170	911.7	912.2	23.2	23.8	65.3	67.1	0	64.216	D1995284.182
12.0	15.6	135.145	135.180	914.0	914.2	23.7	24.6	61.0	62.7	1	62.501	D1995287.185
13.8	18.3	135.105	135.170	912.7	913.2	25.1	26.0	55.7	57.2	0	64.216	D1995287.245
10.0	13.3	135.100	135.215	913.4	913.5	21.7	21.8	86.4	87.1	3	62.255	D1995287.582
9.5	13.2	135.155	135.200	913.0	913.2	21.6	21.8	85.3	85.8	3	62.255	D1995287.641
13.3	14.9	135.150	135.175	914.0	914.2	24.5	25.6	51.5	54.7	1	62.501	D1995288.167
13.6	16.0	135.100	135.165	913.2	913.5	25.6	26.6	51.2	53.5	0	64.216	D1995288.225
10.0	14.5	135.145	135.205	913.5	913.5	22.1	22.2	69.9	70.0	3	62.255	D1995288.564
9.5	395.4	134.400	135.200	913.0	913.0	21.8	22.0	69.4	70.3	3	62.255	D1995288.6227 X/S
14.1	16.0	135.095	135.185	914.9	915.0	23.2	24.1	61.0	61.9	0	64.216	D1995289.148
11.8	16.8	135.140	135.190	914.0	914.5	25.0	26.0	51.7	55.4	1	62.501	D1995289.207

Interne Id 20 (Bangalo)

P	Start	Dauer [sec]	Bed [%]	F0 [%]	F1	F2	F3	F4	F5	AGC0 [V]	AGC1 [V]	Temp [C]	A#H	#R	Ion-Bedeckung
1	9-OCT-1995 04:27:02	565	100.0	99.5	0	0	1	2	0	2.94	4.56	21.8	10	9	TTTTTTTTTF
2	9-OCT-1995 06:10:38	324	85.8	90.3	0	0	1	25	1	3.07	4.92	21.7	4	4	TTTF
3	9-OCT-1995 15:30:43	297	60.4	75.6	0	0	2	42	0	3.07	5.61	22.8	2	2	FT
4	9-OCT-1995 17:04:57	826	100.0	99.3	0	0	2	4	0	2.96	5.50	22.8	14	14	TTTTTTTTTTTTTT
5	9-OCT-1995 18:49:12	276	100.0	24.5	0	0207		1	1	3.11	5.54	22.8			
6	10-OCT-1995 05:38:50	352	100.0	96.0	0	0	1	13	0	3.03	3.23	21.7	5	5	TTTTT
7	10-OCT-1995 18:14:38	627	100.0	99.0	0	0	1	5	0	3.07	5.54	22.9	10	10	TTTTTTTTTT
8	11-OCT-1995 05:06:04	468	100.0	94.5	0	0	1	25	0	3.07	4.88	21.8	7	7	TTTTTTT

XSmin [m]	XSmax [m]	XXmin [m]	XXmax [m]	Pmin [HPa]	Pmax [HPa]	Tmin [C]	Tmax [C]	Hmin [%]	Hmax [%]	K	TT [m]	Output/Kommentar
13.7	16.6	135.105	135.180	912.9	912.9	21.3	21.6	79.4	79.9	0	64.216	D2095282.160
13.5	16.5	135.125	135.175	911.2	911.4	23.3	23.5	69.8	69.9	1	62.501	D2095282.222
10.5	11.2	135.035	135.145	910.9	910.9	21.6	21.6	73.0	73.0	3	62.255	D2095282.558
9.8	205.0	134.400	135.190	911.7	911.7	20.3	20.6	71.1	73.0	3	62.255	D2095282.615? X/S ! zu wenig XS Dat
11.8	15.6	135.165	135.190	911.2	911.2	21.5	21.7	79.0	79.0	1	62.501	D2095283.203
9.6	11.8	135.155	135.195	908.9	909.0	20.0	20.0	88.0	88.0	3	62.255	D2095283.657
11.6	16.0	135.120	135.170	911.7	911.9	23.5	23.8	65.3	67.1	1	62.501	D2095284.184

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Some results of Bangalore PRARE Station
1. Range Full Rate

Station No. HW Name	Passes Jan. 1997 30	31	1	2	3	4	5	Passes	Sum Obs	Noise: [cm]	Remarks
7730 03 Postd-0	6	7	7	7	7	8	7	49	24395	3.47	
7754 05 Neumaye	11	11	11	12	11	12	12	80	47784	4.76	
7704 08 Mater-0	5	4	4	5	4	5	5	32	15274	3.43	
7709 09 Tahiti	4	4	4	4	4	4	4	28	16655	2.96	
7721 10 KokeePa	3	4	4	3	4	4	4	26	14553	3.05	
7722 12 Grblt-0	4	3	4	4	3	4	4	26	12836	3.29	
7728 13 Ny_Ales	13	12	13	11	11	13	11	84	55107	3.76	
7716 15 Maracai	4	1	1	3	4	3	4	20	9628	2.53	
7714 17 Hartebe	-	-	-	4	3	4	4	15	9273	3.19	
7721 20 Kitabe	4	4	3	4	4	3	6	28	13724	3.48	
7758 21 Pasaden	4	4	4	3	4	4	3	26	10573	3.48	
7720 22 UlaanBa	-	3	4	1	3	4	1	16	1439	4.65	
7725 23 Bangalo	4	4	5	3	3	4	4	27	15777	2.77	
7713 24 LaPlata	3	4	2	4	2	2	2	19	7353	2.51	
7710 26 0_Higgi	10	9	9	11	10	8	11	68	37547	6.36	
7703 27 Wettzel	-	-	-	2	5	6	6	19	10071	3.52	
7717 28 Ascebsi	3	4	3	4	5	3	3	25	12262	3.75	
Sum :	78	78	78	83	89	91	91	588	314251	3.90	

Jan 16 09 : 44 1997 MAIL Page 8

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2. Range Normal Point

Station No.	HW Name	Passes Jan. 1997 30	31	1	2	3	4	5	Passes	Sum Obs	Noise: [cm]	Remarks
7730	03 Potsd-0	6	6	7	7	6	8	7	47	1277	0.81	
7754	05 Neumaye	10	11	11	12	10	12	12	78	2303	1.03	
7704	08 Mater-0	5	4	4	5	4	5	5	32	928	0.66	
7709	09 Tahiti_	4	4	4	4	4	4	4	28	1027	0.66	
7724	10 KokeePa	3	4	4	3	4	4	4	26	921	0.65	
7722	12 Grblt-0	4	3	4	4	3	4	4	85	1731	0.98	
7728	13 Ny_Ales	13	12	14	11	11	13	11	85	1731	0.98	
7716	15 Maracai	4	1	1	3	4	3	4	20	623	0.55	
7714	17 Hartebe	-	-	-	4	3	4	4	15	593	0.70	
7721	20 Kitab_	4	4	3	4	4	3	6	28	842	0.80	
7758	21 Pasaden	4	4	4	3	4	4	3	26	632	0.91	
7720	22 UlaanBa	-	2	3	1	3	1	-	10	46	0.95	(1)
7725	23 Bangalo	4	4	5	3	2	4	4	26	962	0.60	
7715	24 LaPlata	3	4	2	2	4	2	2	19	456	0.60	
7710	26 O-Higgi	9	9	9	11	10	8	11	67	1757	1.11	
7703	27 Wettzel	-	-	-	2	5	6	6	19	582	0.83	
7717	28 Ascensi	3	4	3	4	5	3	3	25	779	0.81	
	Sum	76	76	78	83	86	88	90	577	16205	0.87	

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3. Doppler Full Rate

Station No	HW Name	Passes Jan. 1997 30	31	1	2	3	4	5	Passes	Sum Obs	Noise: [cm]	Remarks
7730	03 Potsd-0	6	7	7	7	7	8	7	49	22518	0.12	
7754	05 Neumaye	11	11	11	12	11	12	12	80	48951	0.15	
7704	08 Mater-0	5	4	4	5	4	5	5	32	13800	0.16	
7709	09 Tahiti_	4	4	4	4	4	4	4	28	15661	0.24	
7724	10 KokeePa	3	4	4	3	4	4	4	26	13320	0.22	
7722	12 Grblt-0	4	3	4	4	3	4	4	26	11537	0.09	
7728	13 Ny Ales	13	12	13	11	11	13	11	84	515117	0.09	
7716	15 Maracai	4	1	1	3	4	3	4	20	8799	0.16	
7714	17 Hartebe	-	-	-	4	3	4	4	15	8802	0.19	
7721	20 Kitab	4	4	3	4	4	3	6	28	11890	0.07	
7758	21 Pasaden	4	4	4	3	4	4	3	26	9595	0.12	
7720	22 UlaanBa	-	3	4	1	3	4	1	16	718	0.04	
7725	23 Balgalo	4	4	5	3	3	4	4	27	14646	0.19	
7715	24 LapPlata	3	4	2	2	4	2	2	19	6288	0.10	
7710	26 O_Higgi	10	9	9	11	10	8	11	68	34389	0.11	
7703	27 Wettzel	-	-	-	2	5	6	6	19	9163	0.13	
7717	28 Ascensi	3	4	3	4	5	3	3	25	10961	0.22	
Sum		78	78	78	83	89	91	91	588	2925355	0.15	

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4. Doppler Normal Point

Station No	HW Name	Passes Jan. 1997 30	31	1	2	3	4	5	Sum Passes	Sum Obs	Noise: [cm]	Remarks
7730	03 Potsd-0	6	6	7	7	6	7	6	45	1158	0.009	
7754	05 Neumaye	11	10	10	12	11	12	12	78	2194	0.010	
7704	08 Mater-0	5	4	4	5	4	5	5	32	833	0.014	
7709	09 Tahiti_	4	3	2	3	4	4	4	24	818	0.022	
7724	10 KokeePa	3	3	4	3	2	4	3	22	707	0.020	
7722	12 Grblt-0	4	3	4	4	3	4	4	26	670	0.010	
7728	13 Ny_Ales	12	12	13	11	10	13	10	81	1477	0.010	
7716	15 Marcai	4	1	1	3	4	2	3	18	524	0.017	
7714	17 Hartebe	-	-	-	4	2	4	4	14	501	0.016	
7721	20 Kitab	4	4	3	4	4	3	5	27	727	0.010	
7758	21 Pasaden	3	4	4	3	4	4	3	25	558	0.014	
7720	22 UlaanBa	-	2	-	1	1	-	1	5	17	0.010	(1)
7725	23 Bangalo	4	4	5	3	1	4	4	25	847	0.015	
7715	24 LaPlata	3	4	2	2	4	2	2	19	399	0.012	
7710	26 O Higgi	9	8	9	10	8	7	9	60	1494	0.013	
7703	27 Wettzel	-	-	-	2	5	6	6	19	517	0.011	
7717	28 Ascensi	3	4	3	3	3	3	3	22	599	0.024	
	Sum	75	72	71	80	76	84	84	542	14040	0.014	

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I am extremely thankful to Dr. S. Rangarajan, Director, ISTRAC/MCF for his encouragement and keen interest bestowed on me in bringing out this article. My sincere thanks are due to Mr. A. Karuppaiyan, DGM, SAT-TIC for giving valuable suggestions for the article. My thanks are also due to Mr. V. Jalaramaiah GM, NET-AUG for his guidance.

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K. ELANGO

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Peenya Industrial Estate,
Bangalore - 560058, India.

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Academy News

1. **Prof. Saligram Sinha Memorial Lecture,** organised by the National Academy of Sciences, India, Allahabad, was delivered by Prof. Deepak Pental, Professor of Genetics and Director, Centre for Genetic Manipulation of Crop Plants, University of Delhi, New Delhi, on "*Crop breeding by a combination of conventional and molecular methods : a case study of Brassica species*," in the Botany Department Auditorium of Allahabad University on Saturday, January 10, 1998.

In the end of lecture, Dr. V.P. Kamboj, General Secretary of the Academy & Former Director, C.D.R.I., Lucknow, thanked the speaker and distinguished guests and Prof. P.N. Tandon, President of the Academy & Former Bhatnagar Fellow of A.I.I.M.S., New-Delhi, presented Prof. Saligram Sinha Memorial Lecture Award to Prof. Pental. The Award comprises of a citation, medal and Rs. 5000/-

Lecture was attended by very distinguished scientists like Prof. M.G.K. Menon, Dr. (Mrs.) Manju Sharma, Dr. V.P. Sharma, Prof. U.S. Srivastava, Prof. H.C. Khare, Prof. Alok K. Gupta, Prof B.K. Verma, Prof. R.C. Mahajan, Prof. Anil Kumar and others.

2. **B-Physics and Neutrino Physics Workshop,** was organised by the Mehta Research Institute of Mathematics & Mathematical Physics and the National Academy of Sciences, India, from Jan. 4-8, 1998.

The five day workshop on B-Physics and Neutrino Physics concluded on 8th January with a feeling of enthusiasm amongst the participants. The lectures on B-Physics centered on studying CP- violation in the B-sector, with all the subtle points being discussed. The proposed experiments in B-Physics to be performed at KEK Japan and SLAC, Stanford, U.S.A. were presented and it was pointed out that the current model of elementary particle interaction would be tested. The present model, known as the standard model, has shown remarkable success in explaining several experiments performed in the eighties, notably at CERN, Switzerland and Fermilab at Chicago. However CP-violation has been a long standing puzzle.

Neutrino Physics seems to give some indication that the present standard model may need modification. The neutrinos observed in the atmosphere resulting from the decay of particles seems to give results which do not completely agree with the predictions. The most recent neutrino result were also presented and their implications were thoroughly discussed.

Prof. M.G.K. Menon also delivered a lecture on various opportunities available for basic research which was followed by a discussion. Prof. Menon pointed that one should concentrate on a few areas and produce world class results, if one desires to pursue basic research. He encouraged the young Indian participants to aim high and bring about an exciting research atmosphere in the Institute.

The conference ended with a discussion on future Indian participation in various proposed experiments. There was a unanimous feeling that another Workshop should be held in the year 2000, by which time several new experimental results will be available.

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3. **National Science Day Celebrated** – Two month's long Science Communication Programmes of the National Academy of Sciences, India were concluded on National Scinece Day, February 28, 1998. National Science Day Function was organised by the Academy in the Auditorium of Jagat Taran Girl's Degree College, Allahabad, which was full to it's capacity.

Prof. U.S. Srivastava, Past President of the Academy and Coordinator of Science Communication Programme presided over the function. He emphasized the importance of organising such programmes and expressed that these programmes play vital role in cultivating scientific temper among the budding scientists. He dealt in brief about all these programmes. The Academy organised Science Extension Lectures during January-February, 1998 in Intermediate and Degree Colleges of Obra, Korwa, Sultanpur and several colleges of Allahabad. Distinguished scientists like, Prof. P.N. Tandon, Prof. U.S. Srivastava, Prof. D. Kaul, Prof. H.C. Khare, Prof. Alok K. Gupta, Prof. P.K. Mandal, Prof. S.C. Srivastava, Prof. Vinod Prakash, Prof. P.K. Khare & others delivered lectures. The lectures were attended by large number of students in all the Colleges. State and Local (Allahabad) level Science Exihibition, Quizes and Debates were also organised by the Academy. Mrs. Shefali Saxena of Kendriya Vidyalaya, Dehradun was given the National Academy of Sciences, India-Science Teacher Award, 1998 for her out of the class scientific activities to generate scientific temper amongst the students. This is the only award of its kind in India - given by a National Academy to an Inter College teacher. The Award carries a citation, a plaque and Rs. 5,000/- in cash.

Students from several places of Uttar Pradesh participated in state level science activities. First prize in state level quiz competition was won by the students of Maharshi Patanjali Vidya Mandir, Allahabad, while second prize went to the team of HINDALCO Higher Secondary School, Renukoot.

In state level debate first prize was bagged by GIC Rudrapur (Nainital) and second was given to Maharshi Patanjali Vidya Mandir, Allahabad. Topic of the debate was "Achievements in scinece and technology since independence have met the aspirations of the Indian people".

Several students also participated in local level science activities.

Dr. V.P. Sharma, Director, Malaria Research Centre, Delhi speaking as the Chief Guest of the function, first recalled the contributions of Sir C.V. Raman, whose announcement of the Raman effect long back on 28th February, is now celebrated as Science Day year after year since 1978. He emphasised, with appropriate examples, the fact that most of the progress made in the country in the last 50 years have been due to the efforts in the areas of science and technology. He pointed out that a career in science is a most satisfying which not only can give one a sound way of life but also gives name and fame and is a tool to serve one's countrymen, leading to a better life.

Proceeding was conducted by Prof. Alok K. Gupta, Head, Department of Earth & Planetary Sciences, A.U., Allahabad and General Secretary of the Academy. He also proposed vote of thanks on behalf of the Academy.

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From the very nature of such publication, it is imperative that the authors are as brief and precise in presenting their work as possible. The following restrictions will be imposed :

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(b) Manuscripts should be typewritten in English, double spaced and should be submitted in triplicate. All mathematical expressions should be typed or written clearly in black ink.

(c) The communication should contain a minimum number of tables, figures and photographs. Figures must be drawn in such a way that they can be reduced to one column width (7.5 cm). Figures must be original drawings or exceptionally sharp glossy prints of about manuscript size. The space occupied by the figures/tables/photographs will be at the expense of text, because no LETTER which occupies a space more than 1500 words space may be published.

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Author Year Journal vol. beginning page

White, M.J.D. (1973) Animal Cytology and Evolution, 3rd Ed., Cambridge University Press, London, p. 320 (For Books).

Osgood, C. F. (1977) in Number Theory and Algebra, ed. Zassenhaus, H., Academic Press, New York, p. 321 (For edited Books).

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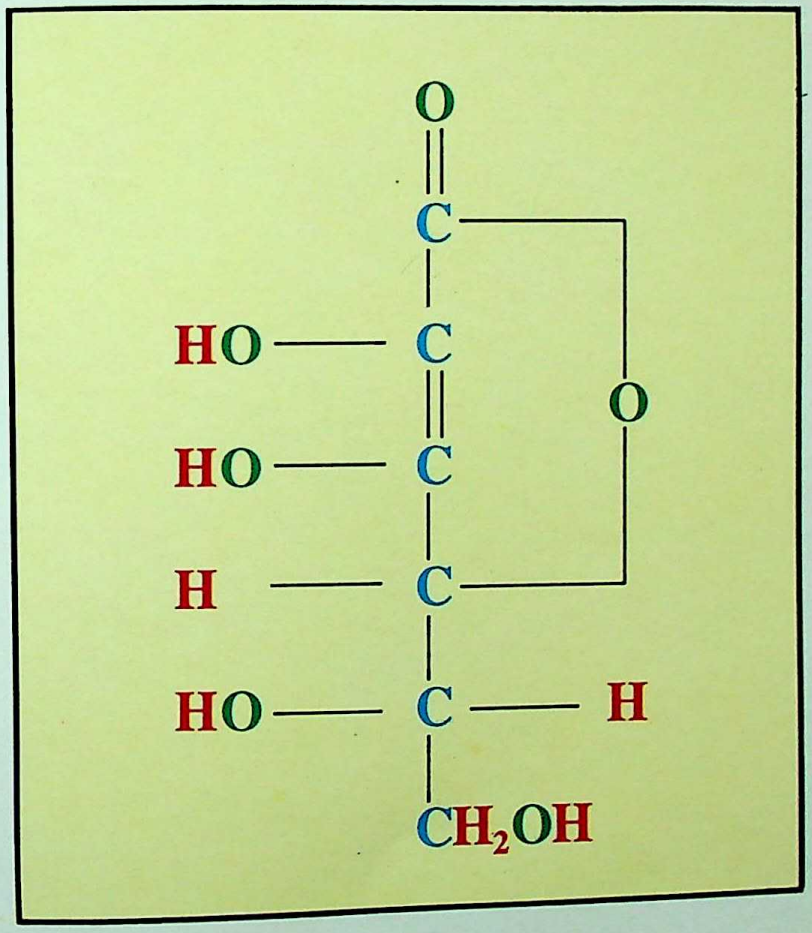

A Monthly Journal of Research

NATIONAL ACADEMY OF SCIENCES, INDIA

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Occasional articles on scientific issues of societal or national interest and news of major scientific events would be welcome.

We will also review books and monographs on scientific subjects and publish the review in this journal. The publication sent for review will be retained in the library of the Academy and one copy of the Journal in which the review is published will be sent to publisher/author free of charge.

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National Academy

March & April, 1998

SCIENCE LETTERS

Vol. 21, No. 3 & 4, 1998

Professor Saligram Sinha Memorial Lecture (January 10, 1998; at Allahabad)

Crop breeding by a combination of conventional and molecular methods : a case study of *Brassia* species

DEEPAK PENTAL

Centre for Genetic Manipulation of Crop Plants, University of Delhi, South Campus, New Delhi - 110021, India.

Crop productivity can be improved by two approaches - by improving agronomic practices (optimal irrigation, fertilizer, proper crop rotation, pathogen and pest management) and by genetic modification of the plant. Both improvement of agronomic practices and genetic modification have played key roles in enhancing crop productivity. My concern in this lecture is mainly with enhancing productivity by genetic modification.

The genetic modification of crop plants is a very ancient activity. The wild relatives of rice and wheat have shattering type of glumes for wide dispersal of the seed. Occassional variants that are non-shattering type are observed in natural populations. One of the key steps, domestication of these plants was conscious or inadvertant selections of types that were non- shattering in habit. In these types, seed would remain on the plant for a long time and could be harvested at will. All plant breeding in the pre-Mendelian times was based on selection at the level of the phenotype. In the post-Mendelian era (which only started after 1900 as Mendel's laws of heredity published in 1866 were not immediately understood), we have gained an unprecedented understanding of how phenotype is influenced by genotype, yet selection at the phenotype level is still a very important method of altering underlying genetics of the plant to enhance productivity and yield stability.

The 1960s saw a tremendous leap in our knowledge of how the genetic material (in most organism DNA) controls its self perpetuation and the biochemical, physiological and development pathways in an organism. By mid 1970s, recombinant DNA techniques were established and as a consequence, the last 20 years have seen a phenomenal increase in our ability to manipulate genetics of organisms. Today genetic information (through cloned DNA) can be transferred between species that are completely unrelated i.e., bacteria and plants.

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The exchange of genetic material, leading to genetic recombination, is a major process by which organisms evolve. In higher organisms, this is brought about by sexual reproduction. However, genetic exchange in crop plants (and for that matter in animals) is limited by sexual incompatibility. As an example, Indian wheat cultivars *(Triticum aestivum)* can be readily crossed with Australian or American wheat cultivars to develop new cultivars. With some difficulty, wheat can be crossed with mroe distant relative like rye of wild species of genus *Triticum* to introgress some useful genes from wild relative to crop species, but recombinant DNA techniques allow the transfer of any gene that is carried by any known organism to wheat thus opening up unprecedented opportunities to manipulate genomes. This is indeed the magic of recombinant DNA techniques. Such exchanges, however, do need lot of experimental manipulation i.e.

1. Genes of potential interest have to be recognized, cloned and characterized,
2. The signal sequences have to be changed, and
3. Methods have to be developed for introduction of foreign DNA into an organism.

In crop plants, foreign DNA can be inserted into cells by use of *Agrobacterium* mediated transformation, by the use of plant protoplasts and by microprojectiles. All the three methods have been used extensively in genetic engineering of crop plants grown on this planer although some are much easier to manage (tobacco, mustard, tomato) as compared to others (wheat, rice etc.).

The protocols for genetic transformation are based on extensive *in vitro* work with plant cells and tissues. Even before recombinant DNA techiques were discovered, plant scientists had shown that somatic cells of plants are totipotent as they have capabilities to divide and give rise to complete plants - thus if foreign DNA (a transgene) is introduced into a cell, an engineered plant (a transgenic) can be raised from such a cell by *in vitro* culture.

By using recombinant DNA technologies, a number of major manipulation have been accomplished. As an example, genes that encode for proteins that are toxic to insect pests have been taken from a bacterium (*Bacillus thuringiensis*) and introduced into tobacco and cotton. The resulting plants are resistant to insect pests. Manipulations have been done to retard senescence so that fruit and vegetable can have prolonged shelf- life. Resistance to viruses has been conferred by overexpressing a part of the virus genome in the susceptible crop. Transgenic crops are undergoing extensive field trials for testing their stability and some of the products are already in the market. However, most of the work remains confined to developed countries.

For the past ten years, along with other colleagues, I have been involved with genetic manipulation of oilseed crops ; mustard (*Brassica juncea*) and its close relative rapeseed (*B. napus*) on transgenics. We have, in our own small way, tried to combine the methods of conventional plant breeding with molecular methods to develop technologies for heterosis breeding in these crops.

In 1985, we decided that in the light of the country importing crores worth of edible oils

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(in 1984-85, this import was worth Rs. 1309 crores), a programme on genetic manipulation of oilseed mustard/rapeseed to increase yield would be very meaningful. In 1986, a Technology Mission on oilseed was set up by Government of India to boost the domestic production. This mission has worked well and the output of oilseed has been increased from 11 million tonnes to 20 million tonnes in 1992-93. However, most of this increase has come from an increased acreage under oilseeds especially mustard. In 1989-90, mustard was grown in 4.9 million hectares while in 1991-92, this area increased to 6.5 million hectares. This increase in area resulted from better procurement prices for edible oils and therefore, was a result in purely economic tinkering. Some increase in yield was also realised by distribution of certified seed and better agronomic conditions including an increase in the area under irrigation.

Very little yield enhancement has come from genetic advancement either by conventional or molecular methods. In fact, a variety named Varuna released in 1964 is still the predominant variety grown in most parts of mustard area in northern India.

Any programme for genetic advancement is, therefore, highly relevant and we have made some progress in developing hybrid seed technologies in oilseed mustard and rapeseed. These could be summarized as following-

1. We have found good combinars in both mustard and rapeseed. Hybrids of these combinars have yield potential of upto 3.5 tonnes/hectare in these comparison to 2.2 tonnes/hectare of varieties like Varuna. In extensive search for combinars, we found that Indian & Indian cultivars of mustard do not give any heterosis but Indian x Russian cultivars give high heterosis.

2. Flowers of most of the crop plants have both male and female parts and in most of the crops, including mutard/rapeseed, the tendency is to self-pollinate. For hybrid seed production, it is important to have male sterile lines. Such lines do not produce any pollen but are female fertile and would set seed with the pollen of the other line. We have developed two male sterility/restorer systems in rapeseed for hybrid seed production and one system for deployment in *B. juncea*. Extensive use has been made of the techniques of somatic cell hybridization to develop agronomically useful male sterile lines and restorer lines.

3. Genetic transformation technologies have been developed for a number of *Brassica* species including mustard/rapeseed and cauliflower. High frequency transformation is now possible with both *Agrobacterium* based vectors and by using simple plasmid vectors with protoplasts.

4. As an alternative to CMS/restorer system, we decided to genetically engineer the good combinars of *Brassica juncea* for hybrid seed production. In 1990, 1992, scientist at Plant Genetic System in Gent, Belgium published two important papers on development of a molecular method for hybrid seed production. Male sterile lines are developed by expressing a ribonuclease (called barnase) under the control of tapetum-specific promoter. In such transgenics, the tapetum tissue degenerates due to porduction of ribonuclease which degrades all the

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mRNA. Consequently, the tapetum cells are not able to provide proper nourishment to microspores which abort providing male sterile lines. Another gene codes for a protein called barstar that tightly binds to barnase and negates its effect. If the male sterile line is crossed with a line carrying barstar gene, the resulting F1 plants will be fully fertile and the farmer can harvest the crop. As we have already identified good combinars in mustard and genetic transformation techniques have already been developed in our laboratory, we have introduced barnase/barstar constructs in *B. juncea* lines. Some of these constructs carry barstar gene modified for its codon usage for high level expression in the tapetal cells.

The hybrid seed production technologies that we have developed are near completion and will be now tested vigorously in multisite trials. If these hybrids show the same promise in such trials as we have seen in our experimental station, we hope that these will eventually move to the farmer's field to bring about a major increase in oilseed production. Only then we will have complete vindication of our approach of combining the conventional and moelcular methods of plant breeding for serving the cause of Indian agriculture.

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Plants used in the preparation of 'Apong' and 'Photika' (country liquor) by 'Mishing' tribe of Assam

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Abstract The 'Mishing' or 'Miri' tribe is confined to remote areas of Upper Assam. In various social functions and festivals country liquors (Apong and Photika) form an indispensable part of social life of the Mishings. Apong is basically prepared by fermenting boiled rice and Photika is prepared by fermenting molasses.

(**Keywords :** Apong/Photika/Epop/Korai/Taasuk)

The 'Apong' used by the 'Mishings' generally fall under two categories : 'Nogin Apong' and 'Poro Apong'. They differ in their tastes, colours and methods of preparation. 'Nogin Apong' is creamy white while 'Poro Apong' is dark green in colour. 'Nogin Apong' does not stay longer than a week, whereas 'Poro Apong' can be preserved for a longer period of time. 'Nogin Apong' is more valued as it is believed to contain low percentage of alcohol and high vitamin contents.

A third variety of liquor called Photika is generally used for commercial purposes.

Mishing inhabited areas of Upper Assam were visited several times and interviewed a large sample of locals including village heads and old people.

Plant materials used for preparation of 'Apong' and 'Photika' were collected with the help of locals and herbarium specimens were prepared. The specimens were subsequently identified at herbaria of Botany Department, Gauhati University and B.S.I., Shillong. Local names of plants were also collected as far as possible. Methods of preparation of 'Apong' and 'Photika' were recorded.

'Nogin Apong' was prepared in the following way :

Husked rice was pulverised to a fine powder with a hand-mill.

Plant materials (listed in the Table1) were pulverised and then mixed with powdered rice and then made into a cake (Epop). Epop was then mixed with previously prepared boiled rice. The mixture was subsequently fermented for a few days in a claypot. After a few days of fermentation, the mixture was strained through a bamboo sieve (Korai). The concentrated extract was generally diluted with cold water before it was used.

The plant species used in the preparation of 'Epop' are presented in Table 1. 'Poro Apong' was prepared in the following way : the preparation of 'Epop' and fermentation procedure were identical with those of 'Nogin Apong'. Ashes of paddy husk were usually added to the bioled rice and then allowed to ferment. The extraction of this particular 'Apong' was done through a funnel- shaped basket prepared from bamboo strips (Taasuk) lined with banana leaves.

'Potika' was prepared by fermentation of molasses alongwith Epop.

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Table 1– Plant species and their parts used in the preparation of 'Epop'.

Botanical Name	Local Name	Part Used
1. *Ageratum conyzoides* L.	Namy In (Mish*), Gundhuwabon (Ass**)	Young shoot
2. *Ananas comosus* Merr.	Konta mati (Mish), Mati Kothal (Ass)	Leaf
3. *Artocarpus heterophyllus* L.F.	Bolang (Mish), Kothal (Ass)	Leaf
4. *Asparagus racemosus* Wild.	Satamul (Mish), Satamul (Ass)	Leaf
5. *Azadirachta indica* A. Juss.	Nim (Mish), Mahanim (Ass)	Leaf
6. *Capsicum annum*	Mirishi (Mish), Jalakia (Ass)	Fruit
7. *C. Minimum* Roxb.	Lukumoni (Mish), Kanjalokia (Ass)	Fruit
8. *Cinnamomum bejolghota* Sweet	Patisunda (Mish), Patishonda (Ass)	Leaf
9. *C. tamala* Nees	Tejpat (Mish & Ass)	Leaf
10. *Clerodendrum colebrookianum* Wall.	Pakum (Mish), Nephaphu (Ass)	Leaf
11. *C. viscosum* Vent.	Labadaba (Mish), Bhetatita(Ass)	Leaf
12. *Commelina benghalensis* L.	Konashimalu (Mish & Ass)	Leaf
13. *Costus speciosus* Smith.	Jamalakhuti (Mish)	Leaf
14. *Cyclosorus extensa* Naud.	Rubji (Mish), Bihlongoni (Ass)	Young leaf.
15. *Euphorbia hirta* L.	Gakhiroti bon (Mish & Ass)	Young shoot
16. *E. pulcherrima* Wild.	Lona Oakkam (Mish), Lalpata (Ass)	Leaf
17. *Heliotropium indicum* L.	Gopatugl (Mish), Hatishuriya (Ass)	Young shoot
18. *Hydrocotyle sibthorpioides* Lamk.	Aggine manimuni (Mish), Shoru manimuni (Ass)	Leaf
19. *Leucas aspera* Spreng.	Namshing guser (Mish), Durun (Ass)	Leaf
20. *Lygodium palmatum*	Kopou dhekiya (Mish & Ass)	Leaf
21. *Mallotus ferrugineus* (Roxb. Muell.)	Moroliya (Mish & Ass)	Leaf
22. *Mangifera indica* L.	Kede (Mish), Aam (Ass)	Leaf
23. *Murraya keeningii* Spreng.	Narashingha (Mish & Ass)	Leaf
24. *Oryza sativa* L.	Apin (Mish), Dhan (Ass)	Husked fruit
25. *Paederia foetida* L.	Bankiribo (Mish), Bhedailata (Ass)	Leaf
26. *Peperomia pellucida* Kunth.	Auni pan (Mish), Goshani pan (Ass)	Leaf
27. *Philogacanthus thyrsiformis* (Hardw.) Mabbr.	Titaphul (Mish & Ass)	Leaf
28. *Ranunculus scleratus* L.	Marsa (Mish), Shuhani (Ass)	Young shoot
29. *Saccharum officinarum* L.	Tabat (Mish), Kuhiyar (Ass)	Leaf
30. *Scoparia dulcis* L.	Youmra Mirishi (Mish), Bon Jalokia (Ass)	Young shoot
31. *Selaginella megaphylla*	Pumugama (Mish)	Entire plant
32. *Sansevieria roxburghiana* Schutt.	Gumuni (Mish & Ass)	Leaf
33. *Tragia involucrata* L.	Pouji (Mish), Churat (Ass)	Leaf
34. *Zingiber officinale* Roscoe	Take (Mish), Aada (Ass)	Under ground stem

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Most of the plants used in the preparation of 'Epop' are harvested from the wild, but a few of them are cultivated near the human settlements. It is interesting to note that some of the plants used have been extensively used to-day as herbal drugs in the treatment of hypertension and diabetes. For example, *Scoparia dulcis* is used in the treatment of diabetes. Similarly *Clerodendrum colebrookianum* is an excellent drug for reducing the hypertension. *Hydrocotyle sibthorpioides* is an immunomodulator.

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Microbiological quality of fresh and smoked *Clarias batrachus* of Manipur

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Abstract Fresh and smoked *Clarias batrachus* avaialble in Imphal market of Manipur during June, July and August 1995, were analysed for microbiological quality. Total count (CFU^{-g}) of bacteria, fungi, *Staphylococcus aureus* and faecal *Streptococci* of fresh and smoked fish were 10^6 *vs.* 10^8, 10^3 *vs.* 10^5, 10^3 *vs.* 10^5 and 10^3 *vs.* 10^4 respectively. Coliform organisms were detected in fresh, but not in smoked samples. In both the samples pathogenic bacteria, *E. Coli* and *Salmonella* were not detected. Microbial counts were slightly more in smoked fish.

(**Keywords** : microbiology/fresh and smoked*Clarias batrachus*)

The hygienic quality of a fish product is judged by its microbiological analysis. Determination of microbiological quality of fish is very important for safeguarding consumers' health. Even very fresh raw material handled and processed immmediately after catch might turn dangerous to human health if handled under unhygienic condition (Iyer)[1]. Contamination of fishery products by coagulase positive *Staphylococcus, Salmonella* and *Streptococci* due to handling has been reported (Sanjeev and Iyer[2], Iyer and Shrivastava[3,4]). Sinha et al.[5], studied the microbial quality of rohu sold in Ranchi town. Reports on the microbiological quality of fishes are scanty in this region. Microbiological quality of fresh and smoked *Clarias batrachus* of Manipur are discussed in this paper.

Fresh and smoked fish of total length 13-20 cm were collected randomly from different fish sellers in the months of June-August, 1995. Whole body was used for the microbiological study. Enumeration of total plate count of bacteria (TPC), fungi (TFC), most probable number (MPN) of coliforms and detection of pathogenic bacteria, *viz.*, *Salmonella, E. coli, Staphylococcus aureus* and faecal *Streptococci* were done as per APHA[6]. TPC were enumerated on nutrient agar, TFC on acidified potato dextrose agar (PDA), coliform number on brilliant green lactose bile (BGLB) broth, *E. coli* on eosine methylene blue (EMB) agar after enriching in BGLB broth, *Salmonella* on brilliant green agar (BGA) after enriching in selenite cystine broth (SCB), *Staphylococcus aureus* on baired parker agar (BPA) following treatment with egg yolk tellurite and *Streptococci* on KF Streptococcal agar containing triphenyl tetrazolium chloride.

Results in Table 1 show that counts of bacteria and fungi in smoked fish were slightly more than those of fresh fish. Lilabati *et al.*[7] reported that smoked *Clarias batrachus* of Imphal market contained 47.58% moisture. In the process of smoking, some flora might have been destroyed. A few flora probably grew later without much competition on the mois-

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Table 1 – Bacterial and fungal count of fresh and smoked *Clarias batrachus* (CFU[8]).

Parameter		Fresh *C. batrachus*	Smoked *C.batrachus*
Total plate count of bacteria	Mean	2.6×10^6	3.8×10^8
	Range	$2.8 \times 10^5 - 8.0 \times 10^6$	$4.5 \times 10^7 - 6.0 \times 10^8$
Total plate count of fungi	Mean	2.8×10^3	2.9×10^5
	Range	$2.0 \times 10^2 - 8.0 \times 10^3$	$4.0 \times 10^4 - 7.4 \times 10^5$
Most probable no. of coliforms	Mean	1.2×10^2	ND
	Range	$9.0 \times 10 - 1.6 \times 10^2$	
Staphylococcus aureus	Mean	2.1×10^3	2.2×10^5
	Range	$3.9 \times 10^2 - 5.0 \times 10^3$	$2.6 \times 10^4 - 6.0 \times 10^5$
Feacal *Streptococci*	Mean	2.4×10^3	1.1×10^4
	Range	$4.0 \times 10^2 - 6.2 \times 10^3$	$1.4 \times 10^3 - 2.2 \times 10^4$
E. coli		ND	ND
Salmonella		ND	ND

Mean value of 12 samples.

ture rich substrate, thus leading to higher counts. TPC of fresh fish is expected to be within 10^4-10^5/g (Nair and Nair[8], Ali *et al.*[9]). But, in the present analysis, it was 10^6g. which might be due to exposure to air for several hours in the market leadings to further contamination. Sinha *et al.*[5] and Yoursef *et al.*[10] also observed similiar findings in the marketed fish. In smoked fish, TPC and TFC were high. Processing caused considerable change in the composition and count of microflora of the fish (Pivovarov *et al.*[11]). The occurrence of moulds to a magnitude of 10^5-10^6/g in fish is a matter of great concern. This flora may be related to a marked degree to the temperature of smoking (Graikoski[12]). The presence of coliform organisms in fresh fish indicates lack of good sanitary practices (Iyer and Pillai, 1971[13]). The incidence of food poisoning organism *Staphylococcus aureus* in fishery porducts in small numbers is not a serious problem, but if its toxin deposited in the product exceeds 4µg/g, food poisoning takes place (Iyer[1]).

Recovery of human enteropathogenic faecal *Streptococci* from the fish indicates the extent of pollution by domestic sewage or faecal contamination. The fish grown in such

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polluted waters may also reflect upon the community health (Nimbargi *et al.*[14]). Contamination of such organisms might also occur during handling and processing. Side effect of *Streptococci* infection causes rheumatic heart, etc. (Rastogi and Kishore[15]). Pahtogenic *E.coli* and *Salmonella* were not detected in fresh as well as smoked fish.

Microbiological quality of the fish provides a better picture about health and hygiene of the product to the consumers and sellers.

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Ternary complexes of some lanthanide ions with cis- 1, 2, 3, 4-cyclopentanetetra carboxylic acid (CPTA) as a primary ligand and 4-pyridine carboxylic acid as a secondary ligand

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Abstract Potentiometric studies are carried out for 1:1:1 ternary complex formation of La^{3+}, Sm^{3+}, Dy^{3+}, Gd^{3+} and Yb^{3+} with cis - 1, 2, 3, 4 cyclopentane tetracarboxylic acid (CPTA) as a primary ligand and 4-pyridine carboxylic acid as a secondary ligand at 25, 35 and 45°C employing modified method of Irving and Rossotti and keeping the ionic strength μ=0.2M ($NaClO_4$). The studies show the formation of ternary complexes of the type M-CPTA-4-PCA where M = La^{3+}, Sm^{3+}, Dy^{3+}, Gd^{3+} and Yb^{3+}. The values of stability constant show the order of stability in terms of metal ions as $Yb^{3+} \approx Gd^{3+} < Dy^{3+} < La^{3+} < Sm^{3+}$. The thermodynamic parameters, free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) have also been evaluated.

(**Keywords** : mixed ligand complexes/1, 2, 3, 4, cyclopentane tetra caraboxylic acid/4-pyridine carboxylic acid/stability constant/thermodynamic parameters)

In continuation to our earlier potentiometric studies[1-7] on mixed ligand complexes of some transition and lanthanide ions with CPTA as a primary ligand, the present work is further extended to some new systems. CPTA is useful in solution varnishes and baths for electroplating. Prostagladins are a group of naturally occurring hydroxy cyclopentane acids derived from fatty acids isolated from mammalian's tissues and are believed to be regulators of various functions such as lipid metabolism, central nervous system, cardio vascular and reproductive physiology. Due to wide range of application of CPTA and pyridine carboxylic acids, it has been preferred to use these compounds as chelating agents.

The present communication deals with stability constant determination of mixed ligand complexes of some lanthanide ions with CPTA as a primary ligand and 4-PCA as secondary by modified method of Irving and Rossotti[8,9]. The formation of mixed ligand complex in a solution containing M, A and B in 1:1:1 ratio, takes place in the following two steps.

$$M + A \rightleftharpoons MA; \qquad MA + B \rightleftharpoons MAB$$

The reaction $M + A \rightleftharpoons MA$ takes place at lower pH and MA is stable at higher pH.

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Perchloric acid (IDPL) : sodium perchlorate $NaClO_4$ (SD fine), CPTA (Matheson, Colemon and Bell Co. USA). 4-pyridine carboxylic acid (Fluka, AG) and other chemicals, AR. Gd. of BDH, Glaxo were used. Solutions of lanthanide metal perchlorate were prepared by dissolving respective metal oxide in calculated amount of perchloric acid till no further salt was soluble. Then the solution was filtered through G-4 crucible of sintered glass and metal ion was estimated as per standard method[10]. CPTA solution was prepared in conductivity water by dissolving calculated weighed quantity of CPTA. Similarly 4-pyridine carboxylic acid solution was prepared. The potentiometric titrations were carried out with the help of Elico model L1-120 with accuracy in pH range 0.5 unit at 25, 35 and 45°C, (± 1°C). Solution temperature was maintained by using thermostatically controlled water bath. Initial volume of each solution to be titrated was kept 50 cc and its ionic strength (μ) was kept 0.2M with $NaClO_4$. The following solutions in duplicate were titrated against 0.2M NaOH at different temperatures.

(a) 0.02M. $HClO_4$ + 0.18M $NaClO_4$.

(b) 0.02M. $HClO_4$ + 0.02M. 4-pyridine carboxylic acid + 0.18M $NaClO_4$.

(c) 0.02M.$HClO_4$ + 0.002M metal perchlorate + 0.002M CPTA + 0.176M $NaClO_4$.

(d) 0.02M.$HClO_4$ + 0.002M metal perchlorate + 0.002 M CPTA + 0.002M 4-PCA + 0.176M $NaClO_4$.

All the solutions were thoroughly shaken and were allowed to equilibrate by keeping for 1 h and each of the mixture was titrated with standard alkali solution (0.2M NaOH) at fixed temperature.

The pK values of 4-pyridine carboxylic acid were calculated using Martell and Chaberek method[11] and are in agreement with the literature values[12]. The values of n (average no. of secondary ligand molecules attached to primary complex) were calculated from the equation[13]

$$n = \frac{(V_3 - V_2)\ (N + E^{\circ})}{(V_0 + V_1)\ \bar{n} H T^{\circ}\ \text{cm}}$$

where

T° cm = Total concentration of metal ion in solution.

N = Normality of alkali used.

E^0 = Initial strength of acid in the system.

V_0 = Total volume of mixture taken initially.

V_1 = The volume of alkali required in the titration of mineral acid (perchloric acid) (Mix A).

V_2 and V_3 are the differences in volume of alkali added between curves (D) and (C) and between (B) and (A) respectively (Fig. 1) at the same pH.

$\bar{n} H$ is average number of protons attached to the secondary ligand at the same pH.

The four titration curves obtained are referred as: (A) acid titration curve, (B) secondary ligand titration curve, (C) primary complex titration curve, (D) mixed ligand complex titration curve. An observation of mixed ligand system shows that no precipitation occurs in mixed ligand system, while a precipitate is formed in the binary system at higher pH. Secondly the mixed ligand curve is displaced from binary complex curve show-

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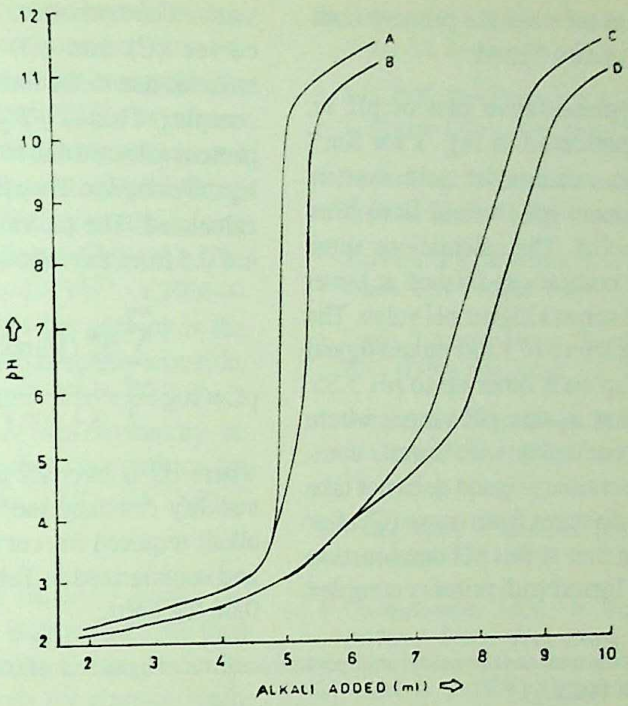
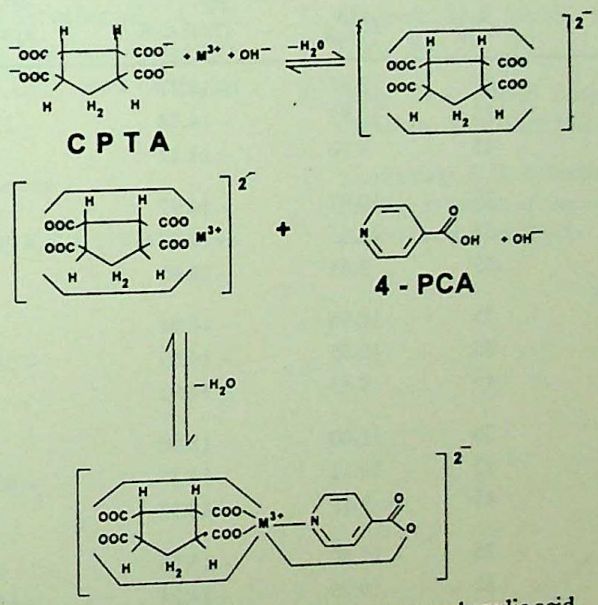


Fig. 1 – Titration curve corresponding to Sm^{3+} – CPTA-4- PCA system.



CPTA = Cis-1, 2, 3, 4, cyclopentane tetra carboxylic acid
4-PCA = 4-Pyridine carboxylic acid.

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ing the interaction between the primary complex and the secondary ligand.

A typical representative plot of pH *vs.* alkali added is presented in Fig. 1 for Sm^{3+} CPTA-4-pyridine carboxylic acid system. Free ligand exponent (pL) values have been calculated at $\bar{n} = 0.5$. The calculations show that the primary complex is formed at lower pH and is stable even at a higher pH value. The primary complex curve (C) and mixed ligand curve (D), overlap each other up to pH 3.35. This indicates that in this pH range, where primary ligand combines with metal, combination of the secondary ligand does not take place, curve (D) diverges from curve (C) after pH 3.35 showing that at this pH combination of the secondary ligand with primary complex starts. The horizontal distance (V_2) between curves (C) and (D) indicates the proton released due to the formation of mixed ligand complex. Thus (V_3- V_2) accounts for the total protons released due to the formation of mixed ligand complex. By using these values, $\bar{n}$ was calculated. The pL values were calculated at $\bar{n} = 0.5$ from the following equation.

$$pL = \log \frac{\sum_{n=0}^{n=j} \beta_n^H (1/\text{antilog } \beta)^n}{T^\circ Cl - \bar{n} T^\circ \text{cm}} \quad \frac{V_0 + V'''}{V_0}$$

where β_n^H is over all practical proton ligand stability constant and V''' is the volume of alkali required for curve (D) at the same pH and summarized in Table 1. The error limit is 0.08 log units.

Table 1 – Stability constants and thermodynamic parameters of mixed ligand complexes at different temperatures ($\mu = 0.2M\ NaClO_4$).

System	Temp. (°C)	K_{MAB}^{MA}	ΔG^0 (kcal mol^{-1})	ΔH^0 kcal mol^{-1})	ΔS^0 (kcal mol^{-1})
Yb^{3+} – CPTA-4PCA	25	10.97	– 14.97	–	–
	35	10.55	– 14.88	– 27.55	– 41.13
	45	9.70	– 14.12	–	–
Gd^{3+} - CPTA-4PCA	25	10.97	– 14.97	–	–
	35	10.55	– 14.88	– 28.64	– 44.68
	45	9.65	– 14.05	–	–
Dy^{3+} - CPTA-4PCA	25	10.95	– 14.94	–	–
	35	10.35	– 14.59	– 28.63	– 45.58
	45	9.63	– 14.02	–	–
La^{3+} - CPTA-4PCA	25	11.00	– 15.00	–	–
	35	10.12	– 14.27	– 40.13	– 83.96
	45	9.15	– 13.32	–	–
Sm^{3+} -CPTA-4CPA	25	11.40	– 15.55	–	–
	35	10.10	– 14.24	– 60.09	– 148.86
	45	8.63	– 12.56	–	–

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In all the systems central metal ions are assumed to acquire the coordination no. of 6. The values of the change in free energy (ΔG°), enthaply (ΔH°) and entropy (ΔS°) have been calculated at three different temperatures and at constant ionic strength $\mu = 0.2M$ ($NaClO_4$) by the temperature coefficient method using Gibbs Helmholtz equations (Table 1). The higher values for ΔS° in the Yb^{3+} - CPTA-4-PCA system indicate that the entropy is the principal driving force for complex formation. The chelates of La^{3+}, Sm^{3+}, Yb^{3+}, Gd^{3+}, Dy^{3+} are formed spontaneously as is obvious by -ve values of δG°. The stability constants of the metal ions follow the order, $Yb^{3+} \approx Gd^{3+} < Dy^{3+} < La^{3+} < Sm^{3+}$ at 25°C.

One of the authors (R.B.G.) thanks Dr. R.L. Rajak and Dr. V. Ragunathan, the then and present Plant Protection Advisor to the Govt. of India respectively for granting study leave and to the management of M.L.N. College, Yamuna Nagar and the other (K.C.G.) to Principal B.S.A. College, Mathura, for providing facilities and to the U.G.C., New Delhi, for financial assistance.

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Biochemically relevant complexes of copper : Synthesis and characterization of some copper(II) heterochelates involving acetoacetanilide, anthranilic acid and heterocyclic nitrogen donors.

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Abstract A new series of mixed-ligand complexes of copper(II) of the composition [Cu(AAA)(AA)(L)], where L = CHPHM, PHM, HTFMP, CTFMP, QNLDA or QNLA, have been synthesized by the interaction of copper(II) chloride dihydrate, acetoacetanilide (AAAH), anthranilic acid (AAH) with the said ligands. The compounds so obtained were characterized by analytical data, molar conductances, magnetic measurements, electron paramagnetic resonance and infrared spectral studies. A square pyramidal geometry for these complexes has been proposed.

(**Keywords** : IR/EPR/magnetic studies/mixed ligand complexes/copper (II))

There is a continuing interest in coordination compounds of cooper(II)[1] with various combinations of heterocyclic nitrogen, thiolate, phenolate and thioether donors because of the coordination of cooper to two histidine sulphur atoms in the blue proteins. The recently developed enzyme[2], Galactose oxidase, contains in its active site a pentacoordinated monomeric copper(II) centre, wherein copper is coordinated to two histidine, two tyrosine and an acetate groups and catalyzes the oxidation of primary alcoholic groups. As it is difficult to incorporate all the donor sites into one ligand, attempts to design mixed-ligand complexes in order to develop small molecular copper analogues involving biologically relevant coordination sphere is of utmost interest. A study of the reactions of copper(II) chloride dihydrate with acetoacetanilide, anthranilic acid and some heterocyclic nitrogen donors, *viz.*, chlorophenira-minemaleate (CHPHM, I), pheniramine-maleate (PHP, II), 2-hydroxy-5-trifluoro-methylpyridine (HTFMP, III), 2-chloro-3-tri-fluoromethylpyridine (CTFMP IV), quinal-dinic acid (QNLDA, V) or quinolinic acid (QNLA, VI) was, therefore, undertaken to isolate hitherto unreported quaternary complexes of copper(II). The heterocyclic nitrogen donors, acetoacetanilide (AAAH) and anthranilic acid (AAH) are structurally shown in Fig. 1.

$CuCl_2.2H_2O$ (B.D.H. Chemical), AAAH, QNLDA, and QNLA (Aldrich Chemical Company) and HTFMP and CTFMP (Ishihara Sangya Kaisha Ltd. Tokyo, Japan), were used as received. All other chemicals used were of A.R. grade.

Complexes were prepared by refluxing combined ethanolic solutions (~70 ml) of $CuCl_2.2H_2O$ (0.01 mol), o-acetoacetanilide,

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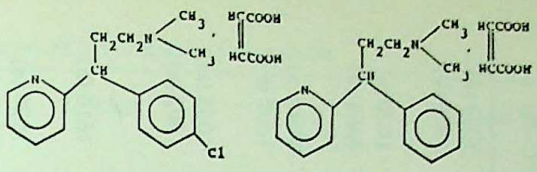
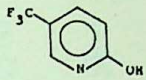


(CWPHM, I)

(PHM, II)



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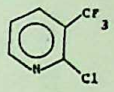

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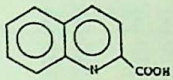
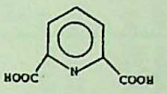
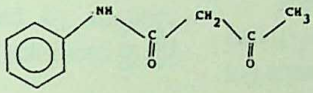


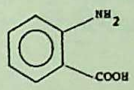
(QNLDA, V)



(QNLA, VI)



(AAAH)



(AAH)

Fig. 1 – Structure of ligands.

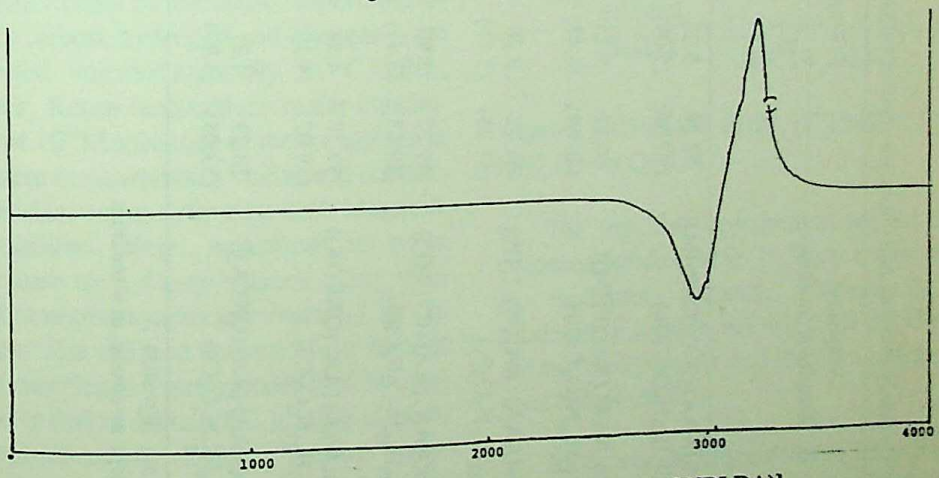


Fig.2 – E.P.R. spectreum of [Cu(AAA) (AA) (QNDLDA)].

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Table 1 – Analytical data and important spectral bands (cm^{-1}) of the synthesized complexes.

Sr. No.	Compound (Empirical formula)	Found (Calc.), %					ν (N–H)	ν (C=O) (Amide carbonyl)	ν (C=O) (Acetyl carbonyl)	ν(COO)	Pyridine ring breathing mode & ν(C=N)
		C	H	N	Cl	Cu					
1.	[Cu(AAA) (AA) (CHPHM)] ($C_{37}H_{39}N_4O_8ClCu$)	57.28 (57.96)	5.27 (5.09)	7.62 (7.31)	4.30 (4.63)	8.72 (8.29)	3266 (a) 3130 (a)	1590 (b)	1573 (a)	1620 (b) 1373 (a)	1033 (a) 1606 (b)
2.	[Cu(AAA) (AA) (PHM)] ($C_{37}H_{40}N_4O_8ClCu$)	60.32 (60.69)	5.25 (5.47)	(7.31 (7.65)	–	8.25 (8.68)	3260 (a) 3410 (a)	1590 (a)	1575 (a)	1615 (b) 1380 (a)	1020 (a) 1608 (b)
3.	[Cu(AAA) (AA) (H[illegible]4P)] ($C_{23}H_{20}N_3O_5F_3$)	51.72 (51.25)	3.20 (3.71)	7.40 (7.80)	–	10.92 (10.38)	3260 (a) 3135 (a)	1595 (a)	1560 (a)	1615 (b) 1368 (b)	1040 (a) 1602 (b)
4.	[Cu(AAA) (AA) (CTFMP)] ($C_{23}H_{19}N_3O_4F_3ClCu$)	49.27 (49.55)	3.70 (3.41)	7.28 (7.54)	6.50 (6.37)	11.83 (11.40)	3270 (a) 3120 (a)	1592 (b)	1565 (b)	1610 (a) 1380 (b)	1035 (a) 1602 (b)
5.	[Cu(AAA) (AA) (QNI.DA)] ($C_{27}H_{23}N_3O_6Cu$)	59.28 (59.07)	4.38 (4.19)	7.29 (7.65)	–	11.19 (11.57)	3280 (a) 3125 (a)	1590 (a)	1570 (a)	1622 (b) 1385 (a)	— 1610 (b)
6.	[Cu(AAA) (AA) (QNLA)] ($C_{24}H_{21}N_3O_8Cu$)	53.29 (53.08)	3.21 (3.87)	7.40 (7.74)	–	11.98 (11.70)	3265 (a) 3160 (a)	1588 (b)	1565 (a)	1620 (b) 1378 (a)	1025 (a) 1612 (b)

a = sh, m ; b = sh, s
sh = sharp; s= strong; m = medium

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Table 2 – Some physical properties of the synthesized complexes.

Sr. No.	Compound	Colour	μ_{eff} (B.M.)	Yield (%)	^ M (ohm^{-1} cm^2 mole^{-1})
1.	[Cu (AAA) (AA) (CHPHM)]	Shiny green	1.80	65	4.5
2.	[Cu (AAA) (AA) (PHM)]	Dirty green	1.78	68	5.5
3.	[Cu (AAA) (AA) (HTFMP)	Green	1.79	53	6.2
4.	[Cu (AAA) (AA) (CTFMP)]	Light green	1.83	50	7.2
5.	[Cu (AAA) (AA) (QNLDA)]	Light green	1.78	62	3.2
6.	[Cu (AAA) (AA) (QNLA)]	Light green	1.84	64	6.8

(0.01 mol), anthranilic acid (0.01 mol) and the appropriate heterocyclic nitrogen donor for 2-3 h. During this time coloured crystals separated. They were filtered by suction, washed several times with ethanol and dried *in vacuo*.

Copper was determined as copper salicylaldoximate by the method reported elsewhere[3]. Carbon, hydrogen and nitrogen were determined microanalytically at C.D.R.I., Lucknow. Room temperature molar conductivities of 10^{-3}M solutions of the complexes in DMF were measured on a Toshniwal conductivity bridge, using a dip type cell. Magnetic susceptibilities were measured at room temperature on a Gouy balance using mercury(II) tetrathiocyanatocobaltate(II) as the calibrant. The infrared spectra of the ligands and the complexes were recorded in KBr/nujol mull on a Perkin Elmer-457 grating infrared spectrophotometer. E.S.R. spectra were recorded on powdered sample at R.S.I.C., I.I.T., Bombay. Electronic spectra of the complexes were recorded in 10^{-3}M DMF solutions on a Shimadzu model UV-160 spectrometer.

The mixed-ligand heterochelates of copper(II) were prepared according to the following equation :

$$CuCl_2.2H_2O + AAAH + AAH + L \xrightarrow[\text{Reflux}]{\text{Ethanol}} [Cu(AAA)(AA)(L)] + 2HCl + 2H_2O.$$

where L = CHPHM, PHM, HTFMP, CTFMP, QNLDA or QNLA.

The resulting compounds are air stable coloured solids (Table 2). They are insoluble in methanol, ethanol, chloroform and moderately soluble in DMF. All the chelates are thermally stable and they do not decompose below 200°C.

Molar conductance values (3.2-7.2 ohm^{-1} cm^2 mol^{-1}) of all the chelates in 10^{-3} M DMF solutions are consistent with the non-

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electrolytic nature of these chelates. The observed magnetic moments (1.78-1.84 BM) of the resulting chelates are indicative of the paramagnetic nature of these chelates with one unpaired[4] electron.

The room temperature X-band E.P.R. spectra of two representative compounds [Cu(AAA)(AA)(CTFMP)] and [Cu(AAA)(AA)(QNLDA)] were recorded on powdered sample at the microwave frequency (9.07 GHz) in the scan range 4000 Gauss. The '*g*' values of 2.111 and 2.122, respectively, were observed for these complexes. The '*g*' values less than 2.3 in the present complexes suggest the covalent nature[5] of metal-ligand bonds in these complexes. The EPR spectrum of [Cu(AAA) (AA)(QNLDA) is shown in Fig. 2.

In the I.R. spectra of the synthesized chelates, two sharp bands at 3260-3280 cm^{-1} and 3120-3160 cm^{-1} are assigned to ν_{as} (NH) and ν_s(NH) for coordinated amino nitrogen of anthranilic acid. The asymmetric and symmetric stretching vibrations of the carboxylate group occur at 1610-1622 cm^{-1} and 1368-1385 cm^{-1} showing a difference of~250 cm^{-1}. This observation[6] suggests that the present complexes contain monodentate carboxylate group of anthranilic acid. The two characteristic absorption bands due to coordinated acetoacetanilide are ν(C=O) (acetyl carbonyl) and ν(C=O) (amide carbonyl). These bands have been observed at 1560-1575 cm^{-1} and 1588-1595 cm^{-1}, respectively, in agreement with the reported results[7].

The ligands CHPHM, PHM, QNLDA and QNLA posses two potential donor sites (i) the ring nitrogen and (ii) the amino nitrogen in cases of CHPHM and PHM or caboxyl oxygen in cases of QNLDA and QNLA. QNLA possesses one more carboxyl oxygen as the third donor site. CTFMP and HTFMP contain only the pyridine ring nitrogen as one of the donor sites.

The characteristic sp^3 ν(C-N)[8] appearing around 1180 cm^{-1} of free CHPHM and PHM remains unchanged in their respective complexes. This indicates the inertness of the side chain nitrogen in bonding. The υ(COO) occurring at ~1670 cm^{-1} in QNLDA and QNLA remains unperturbed in the I.R. spectrum of the corresponding complexes, excluding the coordination possibility of carboxyl oxygen to copper. However, the appearance of ν(C=N) and pyridine ring breathing modes due to ring nitrogen in all the complexes at 1602-1612 cm^{-1} and 1020-1040 cm^{-1}, respectively, suggests the coordination of these heterocyclic ligands through the ring nitrogen[9]. All the complexes do not show band(s) for coordinated water. The overall I.R. data indicates that the heterocyclic donors understudy behave as monodentate ligands. Thus the metal centre is pentacoordinated in all the complexes.

Electronic spectra of two representative compounds, [Cu(AAA)(AA)(PHM)] and [Cu(AAA)(AA)(QNLDA)] exhibit a single broad band at 625-640 nm which probably represents three closely spaced transitions. It has been observed that absorptions in the vicinity of 700 nm suggest 5 or 6 coordinated copper whereas absorptions at ~550 nm indicate 4-coordinated copper[10]. thus the electronic spectra of these complexes do not give information on the geometry. However, based on a criterion proposed by Hathaway et

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al.[11], a square pyramidal structure may be tentatively assigned to these complexes.

The satisfactory analytical data and all the above results suggest that the heterochelates may be formulated as [Cu(AAA)(AA)(L)] where AAAH = acetoacetanilide, AAH = anthranilic acid and L = CHPHM, PHM, HTFMP, CTFMP QNLDA or QNLA.

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Complex formation equilibria of 2,4,-diamino-5 (3,′4,′5,′ -trimethoxybenzyl) pyrimidine, (Trimethoprim) with proton and metal ions

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Abstract The proton-ligand and metal-ligand formation constants of TMP in 50% v/v aqueous methnol medium have been investigated.

(**Keywords** : formation constants/metal ions/ trimethoprim)

Trimethoprim (TMP) 2,4-diamino-5(3,'4,'5,'- trimethoxybenzyl) pyrimidine is a well known drug which exibits antibacterial activity. It is employed as metabolic inhibitor of the bacterial dihydrofolic acid reductase[1]. Although TMP metal derivatives have been described in solid state[2-6] but no information pertaining to the study of complex equilibria of TMP with proton and metal ions in solution is reported in literature. The present investigation deals with the proton- ligand and metal-ligand formation constants of TMP in 50% v/v aqueous methanol medium.

The purity of TMP (m.p. 200°C) was checked potentiometrically and its solution was prepared in methanol. All other chemicals used were of analytical grade. Total volume in each case was 20 ml. An EC digital pH meter with combined glass and calomel electrode assembly was used fo pH measurements (accuracy ± 0.01). The pH titration technique of Irving and Rossotti[7] was used to determine proton-ligand formation constant of the ligand (log K_1^H) and formation constants of metal-ligand complexes i.e. log K_1 and log K_2. The pH values in aqueous methanol medium were corrected[8]. The following mixtures - (a) concentration of HCl (0.0095M), (b)a+concentration of ligand (2×10^{-3}M) and (c) b+ concentration of metal ion (4×10^{-4}M) wsere prepared in 50% v/v aqueous methanol at ionic strength of 0.15 M NaCl at 25 ± 0.1°C and titrated against 0.106 N NaOH potentiometrically.

Molecular orbital calculations indicate that N_1 is the most basic nitrogen atom in pyrimidine- 2,4-diamine and it has long been suggested that protonation takes place predominantly on N_1[9, 10]. The protonated ligand (I) shows ionization of N_1 proton in the pH range 5-9 and the value of log K_1^H as determined by the method of Irving and Rossotti[7] has been found to be of the order of 7.51 as expected.

The scheme of ionization is represented as I $\rightleftharpoons$ II.

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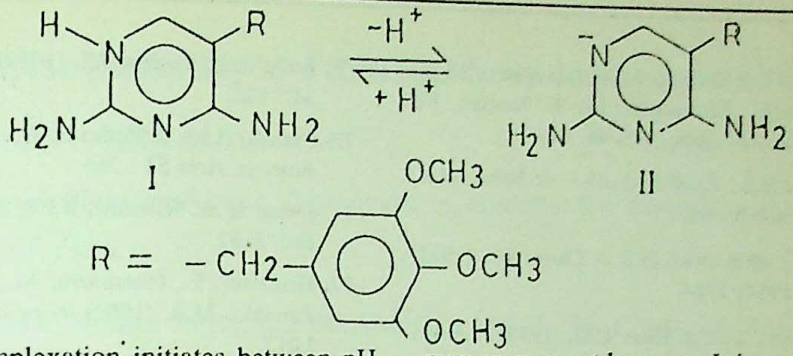

The complexation initiates between pH 3.5-4.0 for Fe^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, VO^{2+} and UO_2^{2+} whereas at about pH 4.2 and 5.8 in case of Zn^{2+} and Cu^{2+} ions respectively. The value of $\bar{n}$ lies between 0 and 1 in case of Mn^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} while between 0 and 2 for Fe^{2+}, VO^{2+} and UO_2^{2+} ions. In case of Mn^{2+}, CO^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}, the value of log K_2 could not be determined due to sudden rise in the $\bar{n}$ values as it tends to unity. This may probably be because of the hydrolysis of these metal ions. The values of log K_1 and log K_2 as determined by standard method[7] are, M(log K_1/log K_2) ; Mn^{2+} (4.88), Co^{2+} (5.53), Ni^{2+}(5.69), Cu^{2+}(3.41), Zn^{2+}(4.53), Fe^{2+} (6.63/5.29), VO^{2+}(5.86/4.63) and UO_2^{2+}(5.43/4.49). The average uncertainity in the log K_1 and log K_2 values is + 0.04. The trend of stability constants as deduced from log K_1 values has been found to be : Fe^{2+} > VO^{2+} > Ni^{2+} > Co^{2+} > UO_2^{2+} > Mn^{2+} > Zn^{2+} > Cu^{2+}. The position of log K_1 values of Cu^{2+} and Fe^{2+} in the sequence is contrary to the expected trend. The higher value of log K_1 in case of Fe^{2+} complexes may be due to the orbital stabilization and additional resonace energy stabilization introduced through a ligand with an aromatic system[11].

The stoichiometry and stereochemistry of the complexes in the solution and solid phase may or may not be same. It is an established fact that the mode of coordination of metal ions in solid compelexes depends on the method of preparation of the complex. In some cases, Cu^{2+} coordinates through N_1 pyrimidinic nitrogen of TMP[12]. However, it has recently been observerd that TMP ligand behaves as monodentate through amino nitrogen atom. The ring nitrogen atom N_1 is not involved in the coordination to metal ion[6] as expected. Further it is interesting to note that pH of the solution at which the complexation of Cu^{2+} starts is greater i.e. 5.8 in comparison to other metal ions. Consequently, in adition to the other facts stated above, pH factor is mainly responsible for the abnormal position of Cu^{2+} in the sequence.

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Rayleigh Taylor instability in a thin film bounded by a porous layer

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Abstract The Rayleigh Taylor stabilty in a finite thickness layer of a viscous fluid bounded below by a densely packed thick porous thick porous layer and above by a rigid surface has been studied subject to linear analysis using approximations in efect similar to lubrication and Stokes approximations. The problem is studied analytically. It is shown that the nature of the linear stability curve is controlled by the slip parameter α and the thickness of the fluid layer h, while its shape is controlled by the ratio of the surface tension to the normal stress.

(**Keywords** : Rayleigh Taylor instability/thin film/porous layer)

The phenomenon of instability of the interface between a heavy fluid supported by a lighter fluid known as Rayleigh-Taylor (here after called RT) instability has been studied extensively starting from Rayleigh[1] and Taylor[2]. Recently Babchin *et al.*[3] and Brown[4] have studied this RT instability problem in one and two-dimensional thin fluid layers analytically using certain approximations. More recently (see Rudraiah *et al.*[5]), this problem has attracted considerable attention because of its natural occurrence and of its importance in studying the dynamics of composite layers (i.e., liquid layer-porous layer) from an industrial and fundamental perspective. From the industrial view point, understanding and controlling the deformation of the interface between a heavy viscous fluid and densely packed porous layer saturated with a lighter viscous fluid provides useful guidelines for manufacture of products free from impurities. Here the RT instability is relevant in the manufacturing process of Resin Transfer Molding (RTM) to remove air bubbles entrapped by the moving material. The other examples of manufacturing processes involving composite surfaces are vulcanised rubber, cured resins, soft contact lenses and resins for solid pahse synthesis. The work of Rudraiah *et al.*[5] pertains to the use of slip condition proposed by Saffman[6] which envisages no flow in the porous media. However many practical problems cited above involve creeping flow governed by Darcy equation in porous layer. In that case instead of Saffman condition one has to use slip condition proposed by Beavers and Joseph[7] (here after called BJ). The problem discussed by Babchin *et al.*[3], in the absence of porous medium and

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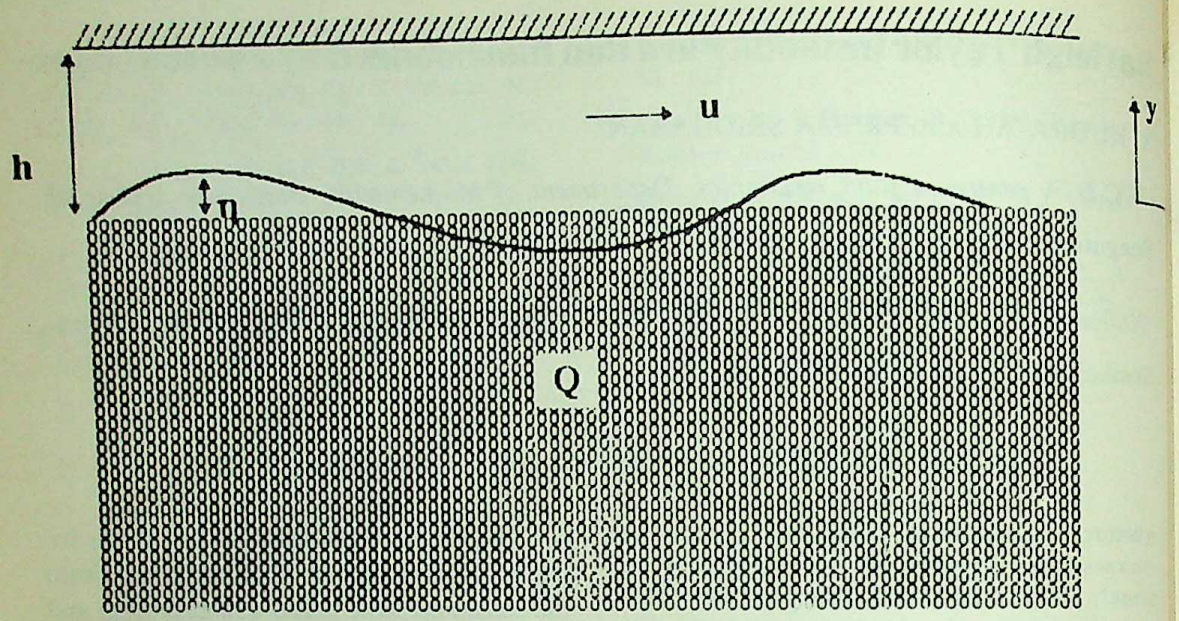

Fig. 1 – Physical configuration.

Rudraiah *et al.*[8], in the presence of porous layer were concerned with heavy fluid of large extent supported by a thin film bounded below by a rigid surface. They have shown that RT-instability exists for long waves. The practical problems discussed above require a situation involving RT stability rather than RT instability for long waves to minimise the defects in the end product. This has motivated us to consider a situation where a heavy fluid confined in a thin film bounded above by a rigid surface and below by a thick densely packed porous layer saturated with lighter fluid. This problem is investigated here anlytically and we show RT stability for long waves in contrast to the RT-instability discussed by Rudraiah *et al.*[8] The object of this work is therefore to study the RT stability of a thin film bounding a porous layer using BJ-slip condition with approximations in effect similar to lubrication and Stokes approximations.

Mathematical Formulation: The physical configuration shown in Fig. 1 consists of two-dimensional horizontal fluid-porous media composite system with a heavy fluid (density ρ_f) in the fluid region of height h supported by a light fluid (density ρ_p) in the porous region of height H. The heavy fluid is bounded above by a rigid material at $y = h$. The co-ordinates x and y indicate horizontal and vertical positions respectively.

The interface between the fluid saturated porous media and the fluid is described by $y = \eta(x, t)$. The velocity components in the x and y directions are denoted by u and v respectively. The fluids are assumed to be Newtonian, viscous and incompressible. Between the two fluids there exists a surface tension γ. The relevant parametes are the fluid viscosity μ, the permeability k of the porous layer, the slip parameter α at the interface, the thickness h of

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the fluid layer, the fluid surface tension γ and the stress $\delta = g(\rho_f - \rho_p)$. The basic equations for the fluid-porous media composite system using lubrication and Stokes approximations[3], are

$$\frac{\partial^2 u}{\partial y^2} = \frac{1}{\mu}\frac{\partial p}{\partial x} \tag{1}$$

$$\frac{\partial p}{\partial y} = 0 \tag{2}$$

$$\frac{\partial u}{\partial x} + \frac{\partial y}{\partial y} = 0. \tag{3}$$

The corresponding boundary and surface conditions are

the no slip condition

$$u = 0 \text{ at } y = h, \tag{4}$$

the BJ[7] slip condition

$$\frac{\partial u}{\partial y} = \frac{\alpha}{\sqrt{k}}(u_B - Q) \text{ at } y = 0, \tag{5}$$

where, u is the velocity of flow parallel to the surface (Fig. 1), u_B is the slip velocity at the permeable surface, $Q = -\frac{k}{\mu}\frac{\partial p}{\partial x}$ is the Darcy velocity, k is the permeability of the porous layer which has the dimension of length squared and α is the slip parameter. Later Rudraiah[8] has shown that the BJ slip condition (5) is valid only in a densely packed porous layer so that the variation of velocity in it can be ignored and the flow is governed by the Darcy equation. In this sense, condition (5) represents the matching of the shear stress at the interface. Therefore the density of the two fluids do not enter in the tangential stress condition, but enters into the normal stress condition (6) through δ.

The normal stress condition at the interface

$$p = -\delta\eta - \gamma\frac{\partial^2 \eta}{\partial x^2} \tag{6}$$

and the kinematic condition at the interface (after linearisation)

$$v(x, 0, t) = \frac{\partial \eta}{\partial t} \tag{7}$$

Solution of (1) using (4) and (5) is

$$u = \frac{h^2}{2\mu}\left(\frac{y}{h} - 1\right)\left(\frac{y}{h} + \frac{\sigma + 2\alpha}{\sigma(1 + \alpha\sigma)}\right)\frac{\partial p}{\partial x} \tag{8}$$

Integration of (3) gives

$$\int_0^h \frac{\partial v}{\partial y}\, dy = -\int_0^h \frac{\partial u}{\partial x}\, dy$$

which leads to

$$v(x, h, t) - v(x, 0, t) = -\int_0^h \frac{\partial u}{\partial x}\, dy$$

But due to no slip condition at the rigid boundary, $v(x, h, t) = 0$.

Hence the above eqn. reduces to

$$v(x, 0, t) = \int_0^h \frac{\partial u}{\partial x}\, dy \tag{9}$$

Eqn. (9) using (8) becomes

$$v(x, 0, t) = -\frac{h^3}{12\mu}\left(1 + \frac{3(\alpha + 2\alpha)}{\sigma(1 + \alpha\sigma)}\right)\frac{\partial^2 p}{\partial x^2} \tag{10}$$

Eqn. (10) using (6) and (7) becomes

$$\frac{\partial \eta}{\partial t} = -\frac{h^3}{12\mu}\left(1 + \frac{3(\sigma + 2\alpha)}{\sigma(1 + \alpha\sigma)}\right)$$

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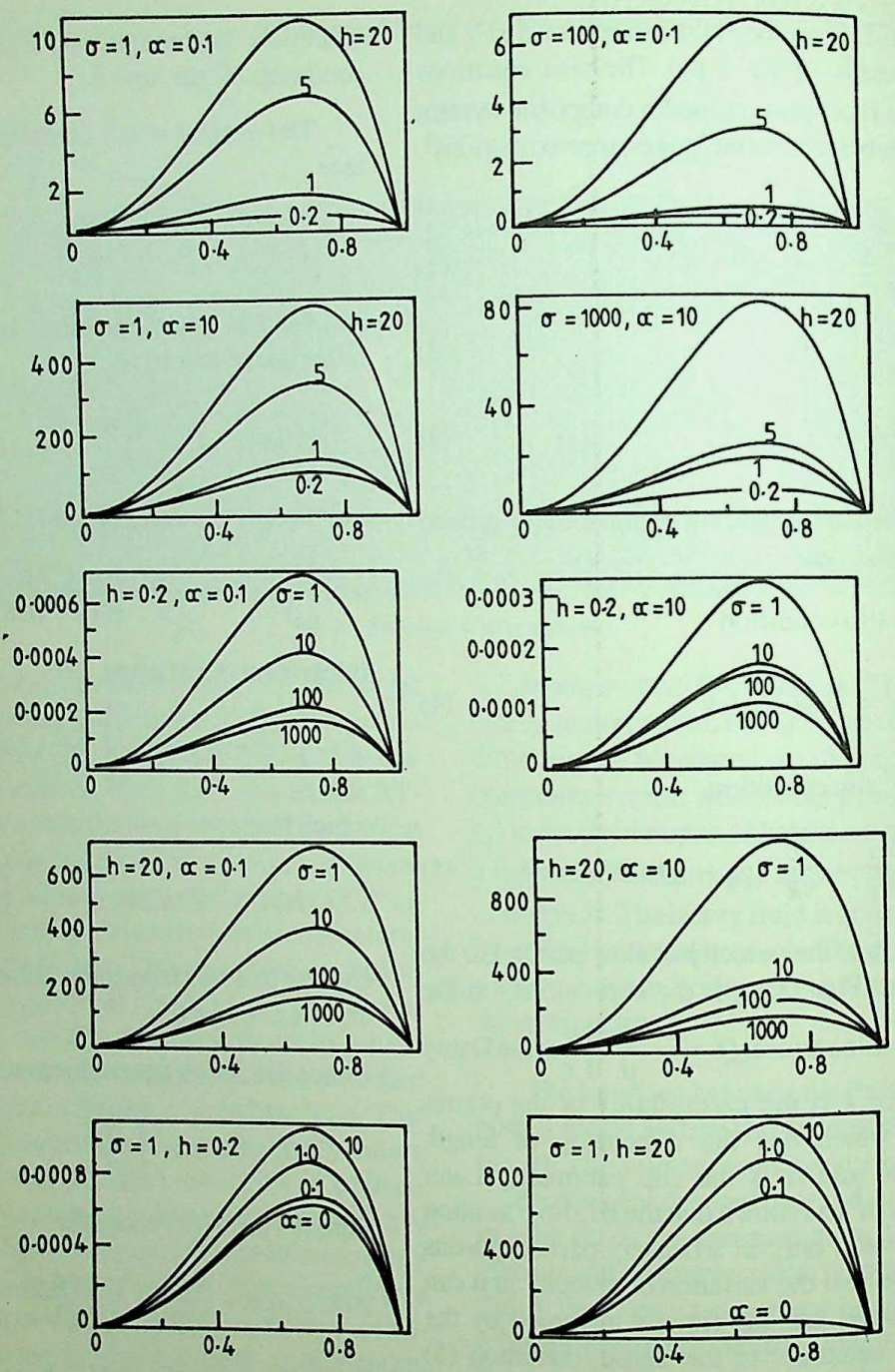

Fig. 2 – Dispersion curves for different values of h, α and σ.

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$$\left(-\delta \frac{\partial^2 \eta}{\partial x^2} - \gamma \frac{\partial^4 \eta}{\partial x^4}\right) \qquad (11)$$

The question of interest is the growth rate of a small periodic perturbation of the interface.

Hence we assume

$$\eta \, \alpha \exp\,(-\, nt + i\, l\, x) \qquad (12)$$

Eqn. (11) using (12) becomes

$$n = \frac{h^3 l^2}{12\,\mu}\left(1 + \frac{3\,(\sigma + 2\,\alpha)}{\sigma\,(1 + \alpha\,\sigma)}\right)(\delta - \gamma\, l^2) \qquad (13)$$

Eqn. (13) in dimensionless form is

$$\hat{n} = \frac{\hat{h}^3\, \hat{l}^2}{12\,\mu}\left(1 + \frac{3\,(\sigma + 2\,\alpha)}{\sigma\,(1 + \alpha\,\sigma)}\right)(1 - \hat{l}^2) \qquad (14)$$

where

$$\hat{n} = \frac{n\,\mu}{\sqrt{\gamma\,\delta}} \qquad \hat{h} = \frac{h}{\lambda} \qquad \hat{l} = l\,\lambda \qquad \lambda = \sqrt{\frac{\gamma}{\delta}}$$

Conclusions: The dispersion relation (14) is computed for different values of $\hat{h}$, α, and the results are depicted in Fig. 2. We found that the shape of the dispersion curve is controlled by the ratio of normal stress to the surface tension γ, while the nature of stability depends on the film thickness h, the slip parameter α and the porous parameter σ. From these figures it is also clear that the increase in α and h increase the frequency while the opposite effect prevails for an increase in σ. The increase in α physically implies the decrease in resistance at the surface leading to the increase in velocity and hence increase in the frequency as evident from equations 7 with 12. Similarly, the increase in σ physically implies the decrease in permeability of the porous medium leading to the decrease in velocity of the flow which in turn decreases the frequency as evidnet from eqn. (7). In other words the increase in α increases the frequency of oscillations at the interface while the increase in σ decreases it. Finally we note that the interface which was unstable for the configuration discussed by Rudraiah *et al.*[5] becomes stable for long waves for the configuaration discussed in the present communication.

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A direct inductive proof of a conjecture due to E Sampathkumar and L Pushpa Latha on the weak domination number of a tree

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Abstract A direct inductive proof, which is more illuminating, of a conjecture that the independent domination number of a tree is at most equal to its weak domination number (due to Sampathkumar and Pushpa Latha) has been provided. A more explicit proof has been given that the weak domination number of a tree is at most equal to its independence number as well by showing that the two numbers are in fact equal for trees having diameter at most four.

(**Keywords** : Graph theory/tree/domination number/independence number)

1. *Introduction*: For standard terminology and notation in graph theory we refer to Harary[1]. New terms and notations shall be specifically defined whenever necessary.

Let $G = (V, E)$ be a simple graph. A subset D of V is said to be dominating in G if for every $u \in V - D$ there exists $V \in D$ such that $uv \in E$ – the least cardinality of a dominating set in G, denoted $\eta(G)$, is called its domination number. This notion was first introduced for graphs, which are not necessarily finite, by Ore[2]. We shall call $K \subseteq V$ a kernel of the graph G if K is both dominating and independent. As noted in Berge[3] this notion was first introduced in game theory under the name 'solution'. However, it was brought into the rigorous graph theoretical formalism by Berge[3] (Chapter 14) with many new fundamental results on the concept in the setting of directed graphs – see Berge and Duchet[4] for recent advancements on this front.

The independent domination number of G, denoted $i(G)$, is the minimum cardinality of a kernel in G. By a theorem of Berge[3] (cf. Chapter 14) one has

$$\eta(G) \leq i(G) \leq \beta_0(G) \tag{1}$$

where $\beta_0(G)$ denotes the independence number of G.

For $u \in V(G)$, let $N_G(u) = \{v \in V(G) - \{u\} : uv \in E(G)\}$ be called the open neighbourhood of u in G, and $d_G(u) = |N_G(u)|$ be called the

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degree of u in G -- the suffix G in these and other such notations will be dropped if G is clear from the context. A vertex of degree 1 will be called a pendant vertex and a vertex of degree at least two is called a support if its open neighbourhood contains a pendant vertex. If v is a support then it is called the support of each pendant vertex in its neighbourhood. The set of pendant vertices in G will be denoted by ¶(G) and the set of supports in G by ¥(G). Note that if G does not have any component isomorphic to K_2 then every pendant vertex in G would have a support.

As in Sampathkumar and Pushpa Latha[5] a set $S \subseteq V(G)$ is a weakly degree dominating (or WDD-) set in G if for every $u \in V(G) - S$ there exists $v \in S$ such that $uv \in E$ and $d(u) \geq d(v)$ (we will then refer to v as a weak image of u).

The weak degree domination number of G, denoted $\gamma_w(G)$, is defined as the minimum cardinality of a WDD-set in G. For a *graph parameter* $f(G)$ defined in terms of cardinalities of subsets of $V(G)$, the subsets S of $V(G)$ for which $|S| = f(G)$ shall be referred to as f-sets in G. In this terminology, we shall denote the set of all $\gamma_w(G)$ -sets by $\mathcal{D}_w^1(G)$.

For any vertex u of a graph $G = (V, E)$ let $N_w(u) = \{v \in V : uv \in E \text{ and } d(u) \geq d(v)\}$. A subset D of V is then a WDD-set of G if and only if $|D \cap N_w(u)| \geq 1$ for every $u \in V - D$. Let the set of all WDD-sets of G be denoted $\mathcal{D}_w(G)$. The following result can be easily established in the same way as its analogue for minimal dominating sets and extends a result of Sampathkumar and Pushpa Latha[5].

Theorem 1 : Let $G = (V, E)$ be any graph and $D \in \mathcal{D}_w(G)$. Then, D is a minimal WDD-set of G if and only if for each $d \in D$ one of the following conditions is satisfied :

(i) $D \cap N_w(d) = \phi$

(ii) $\exists\, v \in V - D$ such that $D \cap N_w(v) = \{d\}$

Proposition 2 : In any graph G. $N_w(u) =$

$$\phi \Rightarrow u \in \bigcap_{S \in \mathcal{D}_w(G)} S$$

Corollary 2.1 : For any graph G having no component isomorphic to K_2, ¶(G) $\subseteq$

$$\bigcap_{S \in \mathcal{D}_w(G)} S$$

Proposition 3 : If M_G denotes the set of vertices with minimum degree $\delta(G)$, then $M_G \cap S \neq \theta$ for any $S \in \mathcal{D}_w(G)$.

Proposition 4 : If u is a pendant vertex of a graph G and if its support v is such that $N_w(v) = \{u\}$ then

$$\gamma_w(G) - 1 \leq \gamma_w'(G - u) \leq \gamma_w(G) . \qquad (2)$$

Proof: Let S be a $\gamma_w(G-u)$-set. Then $v \in S$ and $S \cup \{u\}$ is a WDD-set of G whence we get $\gamma_w(G-u) + 1$. Next, suppose R is a $\gamma_w(G)$-set. If $v \in R$, then $R - \{u\}$ is a WDD-set of $G-u$. On the other hand, if $v \notin R$ then $(R-\{u\}) \cup \{v\}$ is a WDD-set of $G - u$. In either case, we have $\gamma_w(G-u) \leq \gamma_w(G)$. Thus, we have (2).

Proposition 4 implies that if $v_1, \ldots\ldots, v_n$ are the n supports of the n pendant vertices $u_1, \ldots\ldots, u_n$ in a tree H such that $N_w(v_1) = \{u_1\}$ $\forall$ $i \in n = \{1, 2, \ldots\ldots, n\}$ then

$$\gamma_w(G) - n \leq \gamma_w(G - \{u_1, \ldots, u_n\}) \leq \gamma_w(G) \qquad (3)$$

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Proposition 5 : Let $G = (V, E)$ be any graph and u and v be any two vertices such that $x = uv \in E$ and $N_w(u) = \{v\}$ and $N_w(v) = \{u\}$. Then

$$\gamma_w(G) \leq \gamma_w(G - x) \leq \gamma_w(G) + 1 . \qquad (4)$$

Proof : Let S be a $\gamma_w(G)$-set. The given conditions imply that S must contain at least one of u and v. If $u, v \in S$, then clearly S is a WDD-set of G- x too. Hence, let just one of u and v be in S. W.1.o.g., suppose $u \in S$. It is easy to see now that $S \cup \{v\}$ is a $\gamma_w(G - x)$-set so that $\gamma_w(G - x) \leq \gamma_w(G) + 1$.

Next, let R be a $\gamma_w(G - x)$-set. The given conditions imply that $u, v \in R$ whence R is a WDD-set of G as well. This implies $\gamma_w(G) \leq \gamma_w(G - x)$.

Thus, the two inequalities obtained above establish the result.

A new proof of Hattingh-Laskar theorem: Following a conjecture of Sampathkumar and Pushpa Latha[5] the next result has been proved for trees recently.

Theorem 6 : (Hattingh and Laskar[6]) : For any tree T.

$$i(T) \leq \gamma_w(T) \leq \beta_0(T). \qquad (5)$$

We shall give below a short and direct inductive proof of this result as against the rather tedious contrapositive proof originally given in Hattingh and Laskar[6]. Of course, we need some preliminaries.

Lemma 7 : Let $G = (V, E)$ be a finite graph with components $G_1 = (V_1, E_1)$, $G_2 = (V_2, E_2)$, ..., $G_k = (V_k, E_k)$. Then

$$\gamma_w(G) = \sum_{i=1}^{k} \gamma_w(G_i) \qquad (6)$$

Proof : This follows from the fact that a set $S \subset V$ is a WDD-set of G if and only if $S \cap V_1$ is a WDD- set of G_1 for each $i \in n$.

Lemma 8 : If G is a tree whose diameter is at most 4 then $i(G) \leq \gamma_w(G) = \beta_0(G)$.

Proof : Let $\varepsilon(G) = |\P(G)|$ and $\sigma(G) = |¥(G)|$.

Case 1 : diam $(G) = 1$.

Then $G = K_2$ so that $i(G) = \gamma_w(G) = \beta_0(G) = 1$.

Case 2 : diam$(G) = 2$.

In this case, $G = K_{1,n}$ for some integer $n \geq 2$ so that $\varepsilon(G) > 1$ whence we have $1 = i(G) < \gamma_w(G) = \varepsilon(G) = \beta_0(G)$.

Case 3 : diam$(G) = 3$.

In this case, it is easy to see that G has exactly two supports (i.e., $\sigma(G) = 2$), say u_0 and v_0 so that all the other vertices of G are pendant with support u_0 or v_0. Aslo, $u_0v_0 \in E(G)$. By Corollary 2.1, we must have $\gamma_w(G) \geq \varepsilon(G)$. Also, since $\P(G) \in \mathcal{D}_w(G)$ we must have $\gamma_w(G) \leq |\P(G)| = \varepsilon(G)$. Thus, it follows that $\gamma_w(G) = \varepsilon(G)$. But since $\P(G)$ is also a kernel of G, being a maximal independent set of G, we must have $i(G) \leq \varepsilon(G) = \gamma_w(G)$.

Next, notice in this case that $\varepsilon(G) \leq \beta_0(G)$. We shall demonstrate equality here. Let e_1 and e_2 denote the number of pendant vertices at u_0 and v_0 respectively so that $e_1 + e_2 = \varepsilon(G)$ where $e_1 \geq 1$ and $e_2 \geq 1$. It is easy to observe that the only maximal independent sets of vertices in G are $N(u_0) = A_1 \cup \{v_0\}$, $N(v_0) = A_2 \cup \{u_0\}$,

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$¶(G) = A_1 \cup A_2 = V(G) - \{u_0, v_0\}$ where A_1 and A_2 denote respectively the sets of pendant vertices at u_0 and v_0. Therefore, $\beta_0(G) = \max. \{e_1 + 1, e_2 + 1, e_1 + e_2 = \varepsilon(G)\} = \varepsilon(G) = \gamma_w(G)$.

Case 4 : diam $(G) = 4$.

Obviously then $|V(G)| \geq 5$. Let (u_0, u_1, w, v_1, v_0) be a diametral path. Then, the vertex w satisfies the following properties :

(i) $d(x, w) \leq 2 \; \forall \; x \in V(G)$,

(ii) each vertex in $N(w)$ is either a support or pendant and at least two vertices in $N(w)$ are supports of G (i.e., $|N(w) \cap ¥(G)| \geq 2$) *viz.*, u_1 and v_1.

Let $S_i = \{v : d(w, v) = i\}$ for each $i \in \{0, 1, 2\}$. Clearly, $V(G) = S_0 \cup S_1 \cup S_2$ where $S_i \neq \theta$.

Two cases arise for consideration, *viz.*, (a) w is a support, (b) w is not a support.

Subcase (a): $w \in ¥(G)$.

In this case, $S_0 = \{w\} \subset ¥(G)$, $S_1 \subset ¶(G) \cup ¥(G)$, $S_2 \subset ¶(G)$ and hence $V(G) = \bigcup_{i=0}^{2} S_i = ¶(G) \cup ¥(G)$

We claim $\beta_0(G) = \varepsilon(G)$. Let I be any kernel of G. First, suppose $w \in I$. If $I \cap ¥(G) = \phi$ then since $¶(G)$ is a maximal independent set of G we see that $I = ¶(G)$ so that $|I| = \varepsilon(G) = |¶(G)|$. On the other hand, if $I \cap ¶(G) \neq \phi$ then since $|I| = |I \cap ¶(G)| + |I \cap ¥(G)|$ and $|I \cap ¶(G)| \leq |¶(G)| - |I \cap ¥(G)|$ we conclude $|I| \leq |¶(G)| = \varepsilon(G)$. Thus, in either case, we get $|I| \leq \varepsilon(G)$ which implies that $\beta_0(G) \leq \varepsilon(G)$. But since $¶(G)$ is also a kernel in this case we conclude that $\beta_0(G) = \varepsilon(G)$.

Since the set of pendant vertices is a WDD-set of G, $\gamma_w(G) \leq \varepsilon(G)$ and this, together with Corollary 2.1, would give us $\gamma_w(G) = \varepsilon(G)$. Also, since the set of pendant vertices is a maximal independent set we get $i(G) \leq \varepsilon(G) = \gamma_w(G) = \beta_0(G)$.

Subcase (b) : $w \notin ¥(G)$.

In this case, we have $S_0 = \{w\}$ $S_1 = ¥(G) = N(w)$, $S_2 = ¶(G)$ and hence $V(G) = \{w\} \cup ¥(G) \cup ¶(G)$. Again, let I be a kernel of G. Suppose first that $w \in I$. Then, $I \cap N(w) = I \cap ¥(G) = \phi$. Further, since for any pendant vertex u, either u or its support must belong to I we get $¶(G) \subseteq I$. Also, $\{w\} \subset I$ whence $¶(G) \cup \{w\} \subseteq I$. But, since $I \cap ¥(G) = \phi$ and $V(G) = \{w\} \cup ¥(G) \cup ¶(G)$ we conclude that $I = ¶(G) \cup \{w\}$ whence we get $I = \varepsilon(G) + 1$. Next, suppose $w \notin I$. Then, $I \cap N(w) \neq \phi$. Since for any pendant vertex u, either u or its support must belong to I we get $|I \cap ¶(G)| \leq |¶(G)| - |I \cap N(w)$. Therefore, $|I| = |I \cap ¶(G)| + |I \cap N(w)| \leq |¶(G)| = \varepsilon(G)$. Thus, in either case, $|I| \leq \in (G)+1$ and, therefore, $\beta_0(G) \leq \varepsilon(G) + 1$. But since $¶(G) \cup \{w\}$ is a kernel of size $\varepsilon(G)+1$ we conclude that $\beta_0(G) = \varepsilon(G) + 1$.

Further, $¶(G) \cup \{w\}$ is a WDD-set of G as well while $¶(G)$ is not so. This fact, alongwith Corollary 2.1 and the value of $\beta_0(G)$ obtained above, leads to the relationship $\gamma_w(G) = \varepsilon(G) + 1 = \beta_0(G) \geq i(G)$.

The proof is seen to be complete.

The various facts mentioned in the proof of Lemma 8 are summarised below.

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Observation 9 : Let G be a tree of order $n \geq 2$. Then, (*i*) diam $(G) = 1 \Rightarrow i(G) = \beta_0(G) = \gamma_w(G) = 1$: (*ii*) diam $(G) = 2 \Rightarrow i(G) < \beta_0(G) = \gamma_w(G)$: (*iii*) diam $(G) = 3 \Rightarrow i(G) = \beta_0(G)$ $(= \gamma_w(G))$ if and only if $n = 4$: (*iv*) diam$(G) = 3$ and $n > 4 \Rightarrow i(G) < \beta_0(G) = \gamma_w(G) =$ diam (G); diam $(G) = 4 \Rightarrow i(G) < \gamma_w(G) = \beta_0(G)$.

Proposition 10 : For any tree T, $i(T) \leq \gamma_w(T)$.

Proof: Invoking Lemma 8, the validity of the result may be easily verified for all trees of order ≤ 5. Hence, we prove the result by induction on the orders of trees.

Suppose the result is true for all trees of orders less than that of a given tree T.

Case 1 : $\exists\ S \in \mathcal{D}_w^0(T)$ containing a support u_0.

Let $T' = T - \{u_1, u_2, \ldots\ldots, u_n\}$ where $u_1, u_2, \ldots\ldots, u_n$ are the pendant vertices with support u_0. Then $S - \{u_1, u_2, \ldots\ldots, u_n\} = R \in \mathcal{D}_w(T')$ so that

$$\gamma_w(T') \leq \gamma_w(T) - n. \qquad \text{(A1)}$$

Let I be an $i(T')$-set. If $u_0 \in I$, then I is a kernel of T. If $u_0 \notin I$, then $I \cup \{u_1\ u_2, \ldots\ldots, u_n\}$ is a kernel of T. Thus, in any case, we must have

$$i(T) \leq i(T') + n. \qquad \text{(B1)}$$

Also, since T' is a tree having lesser number of vertices than those in T it follows from the induction hypothesis that

$$i(T') \leq \gamma_w(T') \qquad \text{(C1)}$$

It is now easy to see that (A1)-(C1) together imply the result in this case.

Case 2 : $S \in \mathcal{D}_w^0(T) \Rightarrow S \cap ¥(T) = \theta$

Let u_1, v_1 be two antipodal vertices of T. Then, clearly, $u_1, v_1 \in ¶(T)$. Let u_0, v_0 be their respective supports.

If $u_0\ v_0 \in E(T)$ then diam $(T) = 3$ and therefore the result follows from Lemma 8.

Next, suppose u_0 and v_0 are not adjacent in T. Let $P = (u_1, u_0\ w_1, w_2, \ldots\ldots\ldots w_t, v_0, v_1)$ be the unique diametral path between u_1 and v_1. We consider two subcases here.

Subcase 2.a : w_1 is a support.

Then, by assumption, $w_1 \in T - S$. Consider $T' = T - \{u_0, u_1, \ldots\ldots, u_n\}$. Then, T' is a tree with $|V(T')| < |V(T)|$ and $S - \{u_1, u_2, \ldots\ldots, u_n\} \in \mathcal{D}_w(T')$. Therefore,

$$\gamma_w(T') \leq \gamma_w(T) - n. \qquad \text{(A2)}$$

Next, let I be a $i(T')$-set If $w_1 \in I$, then $\cup \{u_1, u_2, \ldots\ldots, u_n\}$ is a kernel of T. If $w_1 \in$ then $I \cup \{u_0\}$ is a kernel of T. Thus, in any case we must have

$$i(T) \leq i(T') + n. \qquad \text{(B2)}$$

Also, by induction hypothesis we get

$$i(T') \leq \gamma_w(T') \qquad \text{(C2)}$$

Thus, (A2), (B2) and (C2) imply the result in this case.

Subscase 2.b : w_1 is not a support.

In this case, let $T' = T - N[u_0]$ where $N[u_0] = \{u\} \cup N(u)$. Again, two cases arise.

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Subscase 2.b.1 : $w_1 \in S$.

If $t = 1$, then diam $(T) = 4$ and the result follows from Lemma 8. If $t > 1$, w_1 would be the only weak image of w_2 in $T - S$ in which case $(S - \{u_1, u_2, \ldots\ldots, u_n, w_1\}) \cup \{w_2\} \in \mathcal{D}_w(T')$ -- note that this statement is valid even when $w_2 \in S$.

Subscase 2. b. 2 : $w_1 \in S$.

In this case, there must exist $w' \in S$ such that w' is a weak image of w_1. Since all other neighbours of w_1 are supports and hence must be in $T - S$ it is easy to see that $w' = w_2$. Therefore, $w_2 \in S$ in this case so that $S - \{u_1, u_2, \ldots\ldots, u_n\} \in \mathcal{D}_w(T')$.

Thus, in either subcase we must have

$$\gamma_w(T') \leq \gamma_w(T) - n. \qquad \text{(A3)}$$

Next, let I be a $i(T')$-set. Then $I \cup \{u_0\}$ is a kernel of T whence

$$i(T) \leq i(T') + 1 \leq i(T') + n. \qquad \text{(B3)}$$

Hence, by invoking Lemma 7 and the induction hypothesis, we get

$$i(T') \leq \gamma_w(T'). \qquad \text{(C3)}$$

(A3), (B3) and (C3) together establish the result.

Proposition 11 : For any tree T, $\gamma_w(T) \leq \beta_0(T)$.

Proof : The result may be easily verified for all trees of orders ≤ 5 using Lemma 8. Let the result be true for any tree T' whose order is less than that of an arbitrarily given tree T. Let u_1, v_1 be any two antipodal vertices of T, with u_0, v_0 as their respective supports.

Case 1 : $u_0 v_0 \in E(T)$.

Then diam $(T) = 3$ and hence the result follows from Lemma 8.

Case 2 : u_0 and v_0 are nonadjacent in T.

Let $P = \{u_1, u_0, w_1, w_2, \ldots\ldots, w_t, v_0, v_1\}$, $t \geq 1$, be the unique $u_1 - v_1$ diametral path. Let $T^+ = T - \{u_0, u_1, \ldots\ldots, u_n\}$. Clearly, T' is a tree. Let S be $\gamma_w(T)$-set.

If $w_1 \notin S$, then $S \cup \{u_1, u_2, \ldots\ldots u_n\}$ is a WDD-set of T. On the other hand, if $w_1 \in S$ then two subcases arise: (*i*) If there is no $w' \in T' - S$ such that w_1 is its unqiue weak image, then clearly $S \cup \{u_1 u_2, \ldots\ldots, u_n\}$ is a WDD-set of T. (*ii*) Suppose there exists $w' \in T' - S$ such that $N_{wT'}(w) = (w_1\}$. This implies that $w = w_2$ since all other neighbours of w_1 are supports or pendant vertices, P being a diametral path and every pendant vertex at w_2 belongs to S alone. Therefore,

$d_{T'}(w_1) \leq d_{T'}(w_2)$:

$d_T(w_1) = d_{T'}(w_1) + 1$,

and $d_{T'}(w) = d_T(w)$

for every other vertex w of T'. If $d_{T'}(w_1) < d_{T'}(w_2)$, then $S \cup \{u_1 u_2, \ldots\ldots, u_n)$ is a WDD-set of T. If $d_{T'}(w_1) = d_{T'}(w_2)$ then $(S - \{w_1\}) \cup \{w_2\} \cup \{u_1, u_2, \ldots\ldots\ldots, u_n\}$ is a WDD-set of T. We find in each case

$$\gamma_w(T) \leq \gamma_w(T') + n. \qquad \text{(A4)}$$

Next, let I be a $\beta_0(T')$-set. Then, $I \cup \{u_1, u_2, \ldots\ldots, u_n\}$ is a kernel of T. Therefore,

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$$\beta_0(T) \geq \beta_0(T') + n. \qquad \text{(B4)}$$

Also, by induction hypothesis, we have

$$\gamma_w(T') \leq \beta_0(T') \qquad \text{(C4)}$$

(A4), (B4) and (C4) together establish the result.

Propositions 10 and 11 together establish the Hattingh-Laskar theorem (*viz.*, Theorem 6).

3. *Concluding Remarks and Scope* : In Sampathkumar and Pushpa Latha[5], an applic-tion of the notion of strong (weak) degree domination in graphs has been mentioned in the context of mobile traffic control on a city road network. However, if the number of roads at a junction ("traffic circle") u is at least the number of roads at an adjacent junction v then the situation when u needs to be preferred to v for letting the vehicles move from u towards v requires the entire city road network to be viewed as a symmetric diagraph in which each arc (x, y) is to be associated with a weight $g(x, y)$ representing some entity (such as the number of vehicles coming from v towards x, *a priori* knowledge of the number of roads meeting at each of the neighbours of x or "expected general traffic condition" of the roads leading towards them on the part of the driver of every vehicle arriving at the junction x for making a comparative choice of y to traverse the road (x, y), etc.) that governs the preference to x over y in choosing the arc (x, y) for effecting the traffic flow. On the other hand, a relevant problem, where use of the notion of strong degree domination applies, is to identify a minimum number of road junctions in the network at each of which the minimum of the "forward traffic load" $\sum_{y \in N(x)} g(x, y)$ and the "reverse traffic load" $\sum_{y \in N(x)} g(x, y)$ exceeds a prescribed global threshold t for such weights assigned to the junctions in the network so as to deploy necessary special traffic control mechanisms (such as traffic police) there. In such a network, the concept of weak degree domination arises when it is required to select a set D of road junctions in the network such that for every junction u not in D the vehicles arriving at u have a choice of a junction v in D adjacent to u such that max. $\left\{ \sum_{y \in N(v)} g(v, y), \sum_{y \in N(v)} g(y, v) \right\}$ is less than certain prescribed global threshold s for such weights assigned to the junctions in the network. These considerations lead to many new notions and problems of practical importance in graph theory which will be attempted elsewhere.

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Effect of dietary vitamin C on survival and moulting of *Macrobrachium rosenbergii* (de Man) larvae reared upto stage V

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Abstract : The effect of dietary vitamin C (99.7% pure, Loba Chemie, Mumbai) on the survival and moulting of *M. rosenbergii* larvae was investigated. Five diets; SDC-25, SDC-75, SDC-125, SDC-175 and SDC-225 containing powdered vitamin C @ 25 mg, 75 mg, 125 mg, 175 mg, and 225 mg per 100 g diet respectively were fed to different groups of larvae and the results were compared with the control (SD) receiving no vitamin C. Survival was recorded after 15 days. Moulting rate was calculated after counting the moults in each aquarium on a day-to-day basis. The highest survival (90%) was obained with diet SDC-175 ($p < 0.01$), while the control recorded 50% survival. Moulting was poor (60 to 70%) in control and 25 mg and 75 mg per 100g feeding trials.

(**Keywords :** vitamin C/larvae/*M. rosenbergii*/survival/moulting)

Dietary essentiality of vitamin C in feed has been studied for eels, shrimps, catfishes, salmonids and carps[1-6]. Prawn cannot synthesize this vitamin and hence supplementation is essential. In general vitamin C causes reduced growth, abnormal body colour, disease susceptibility and higher mortality[7-18]. Vitamin C plays a vital role in enhancing growth, feed efficiency, resistance to stress and skin coloration[19-25].

The present study was undertaken to evaluate the effects of graded levels of vitamin-C (see cover page) on the survival and moulting of larval stages of *M. rosenbergii* reared up to stage V.

The larvae (average weight; 23 microgram per 100 larvae) were obtained from CIFE's freshwater prawn hatchery, Mumbai and kept in glass aquaria (60 × 30 × 30 cm) filled with 35 litre of bore-well water. Aeration was supplied through oil-free air compressor throughout the experimental period. Fifty per cent of water in the aquaria replaced every day. During the experimental duration dissolved oxygen, pH, alkalinity and temperature ranged from 5.2 to 5.7 ppm, 7.5 to 8.1, 220 to 260 and 21° to 25°C respectively. Larvae were fed in four replicates with a basal diet (Table 1) containing vitamin C @ 25 mg (D_2), 75 mg (D_3), 125 mg (D_4), 175 mg (D_5) and 225 mg (D_6) per 100 g diet and the results were compared with the control (D_1). In feeding trial D_4, D_5 and D_6 all the larvae reached stage V within 15 days (Table 2). Survival ranged from 50% to 90% and moulting from 60% to 100%. In treatments D_4, D_5 and D_6

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Table 1– Basal composition of diets (D_1-D_6).

Diet	Code	Composition (%)											
		Cas.	Cellu.	Gel.	Cod.	Vit.	Suc.	Dex.	Egg	Yeast	Cal.	Phos.	Vit.C
D_1	SD (control)	32	32.000	8	5	1	4	6	10	1	0.5	0.5	–
D_2	SDC-25	32	31.975	8	5	1	4	6	10	1	0.5	0.5	25
D_3	SDC-75	32	31.925	8	5	1	4	6	10	1	0.5	0.5	75
D_4	SDC-125	32	31.875	8	5	1	4	6	10	1	0.5	0.5	125
D_5	SDC-175	32	31.825	8	5	1	4	6	10	1	0.5	0.5	175
D_6	SDC-225	32	31.775	8	5	1	4	6	10	1	0.5	0.5	225

Cas. = Casein; Cellu. = Cellulose; Gel. = Gelatin; Cod. = Cod liver oil;
Vit. = Vitamin mixture (devoid of vitamin C); Suc. = Sucrose; Dex. = Dextrin;
Egg = Egg yolk powder; Yeast = Yeast Extract Powder; Cal. = Calcium; Phos. = Phosphorus
Vit. C = Vitamin C (mg %)

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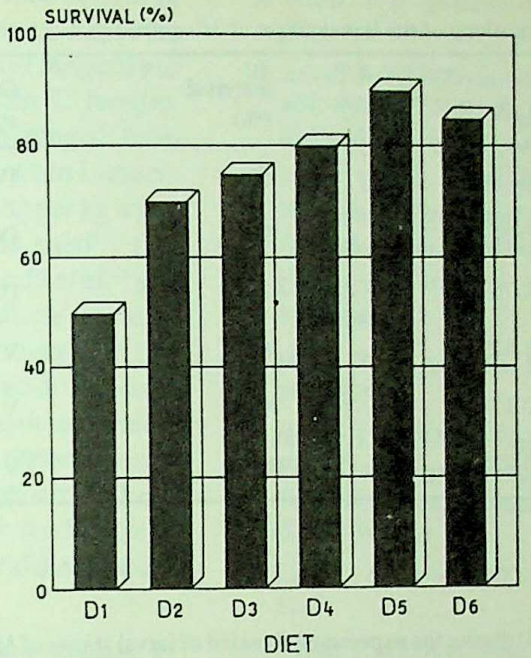

Fig. 1– Survival percentage of the larvae of *Macrobrachium rosenbergii* fed diets having different concentrations of vitamin C.

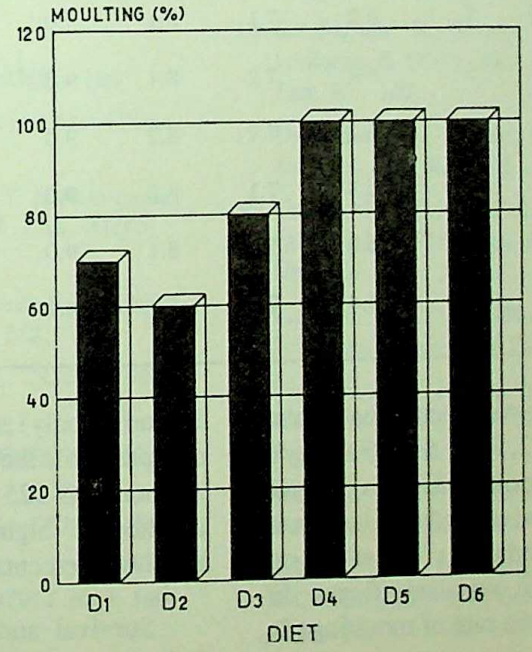

Fig. 2– Percentage of moulting of *Macrobrachium rosenbergii* larvae fed diets having different concentrations of vitamin C.

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Table 2– Survival and moulting of the larval stages of *M.rosenbergii.*

Diet	Code	Survival (%)	Growth stages	Moulting (%)
D_1	SD (Control)	50	IV stage	70
D_2	SDC-25	70[a]	IV stage	60
D_3	SDC-75	75[a]	IV & V stage	70
D_4	SDC-125	80[a]	V stage	100[a]
D_5	SDC-175	90[a]	V Stage	100[a]
D_6	SDC-225	85[a]	V stage	100[a]

a = $p < 0.01$

Table 3 – Salinity (in ppt) during the experimental period of larval stages of *M. rosenbergii* fed diets ($D_1 - D_6$).

Diet	Code	1st Day	3rd Day	5th Day	7th Day	9th Day	11th Day	13th Day	15th Day
D_1	SD (Control)	5	6.2	7.1	8.1	9.0	9.0	10.1	11.0
D_2	SDC-25	5	6.4	7.2	8.1	9.0	9.0	10.1	11.0
D_3	SDC-75	5	6.2	7.1	8.2	9.0	9.0	10.1	11.3
D_4	SDC-125	5	6.3	7.1	8.0	9.0	9.1	10.2	11.8
D_5	SDC-175	5	6.0	7.2	8.1	9.0	9.1	10.1	11.0
D_6	SDC-225	5	6.4	7.2	8.1	8.9	9.1	10.4	11.3

survival and moulting were better than that of D_1, D_2 and D_3 (Table 2, Fig 1 & 2). Salinity of the medium during the experiment is shown in Table 3. Both the survival and moulting rates were statistically tested using 't' test and one way ANOVA. There was significant difference ($p < 0.01$) in the rate of moulting (D_4, D_5 and D_6 only) and survival (all tratments) in comparison to the control. Supplementation of vitamin C @ 125 mg per 100g diet and above resulted in higher survival and increased moulting percentage.

Survival and moulting rate have been linked to environmental conditions and feed-

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ing strategy[26-29]. An optimum requirement of 650 to 750 mg of vitamin C per kg diet in the early part of the life of *Cirrhinus mrigala* has been reported[5]. Dietary vitamin C requirements for *Penaeus japonicus* ranged from 3,000 to 10,000 mg per kg diet when L-ascorbic acid was used[19,20] and 100 mg per kg when Mg-L-ascorbate-phosphate was used[25]. Our results tally with those of Magarelli *et al.*[24] and Lightner *et al.*[22]. Phromkunthong *et al.*,[30] reported histopathological changes and impaired growth in ascorbic acid deficient grouper, *Epinephelus malabaricus*. Since, vitamin C is an important dietary factor regulating growth, hatching time, survival and moulting rate, it is suggested that addition of vitamin C in larval and post-larval diets should be given priority.

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Science News

1. Against the wall

Theory suggests that when a liquid makes contact with a solid wall, the atoms and molecules in the liquid become layered adjacent to the wall. Theory is one thing but actually 'seeing' these layers is another, which until now has not been possible. But using a sensitive technique to measure X-Ray scattering at the buried interface between liquid gallium and a diamond single crystal surface. Huisman *et.al.*, have detected pronounced layering in the liquid density profile, decaying exponentially with distance from the wall. The layer spacing is characteristic of a plane of upright gallium dimer in solid α gallium suggesting that the liquid adopts a solid like structure near the wall.

Nature, 27 Nov; 1997.

2. Confused fish

Upto 60% of male fish in some British rivers have developed significant female characteristics because of chemicals in effluent that mimic the horomone oestrogen, a study commissioned by Environment Agency suggests. Researchers from Brunel University found a direct correlation between the concentration of sewage in rivers and the severeity of feminisation in male roach - including eggs in the testes.

New Scientist, 2118, Jan, 1998.

3. Green continent

Antarctica will be safe from mining and oil exploration for 50 years, after an environmental pact drawn up seven years ago finally became international law last week. All 26 member nations of the Antarctica Treaty have now ratified the Madrid Protocol.

Opposition to the mining ban in the US and Japan held up the law for five years. The pact also sets strict environmental standard for researchers, who must take all their waste with them when they leave the continent.

New Scientists, 2118 Jan, 1998.

4. Sound of Dinosaur

By now most of us are aware what dinosaur looked like. To find out what this 30' long rare duck bill dinosaur sounded like, computer scientists at Sandia National Laboratories in Albuquerque are using special software which analyses 350 CAT scan images of a Parasaurolophus skull that was excavated last year in north western New Mexico. The software is helping scientists map out the intricate network of air passageways within the dinosaur's skull. Based on this the scientists will create computer simultions of the sound that this dinosaur produced due to its unusual skull. Its trombone-like crest contained hollow tubes that enable it to produce low pitched mating and warning calls. But to know what these calls sounded like, we'll have to wait. But then it is worth waiting to hear sounds that haven't been heard for some 75 million years.

Science Reporter, 44, Aug. 1997.

5. Magnetism makes sense

Many animals are known to be able to sense magnetic fields, but the receptors underlying this ability have been remarkably dif-

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ficult to find. Fish of the salmon family may use variations in the intensity of the earth's magnetic field to guide their oceanic migration. A new study of the magnetic sense of the rainbow trout, *Onchorhynchus mykiss* not only demonstrates behavioural and neural responses to changes in magnetic intensity, but also identifies an area in the nose where candidate magnetoreceptors are located, tracks the pathway from these cells to the brain, and demonstrates that the system is associated with a learned response to magnetic fields.

Nature, 27 Nov., 1997,

6. Sulphur surprises

Under the stresses of high pressure and extreme density, familiar elements can adopt unfamiliar properties. Sulphur, for instance, is normally an insulator, but at high pressure is known to be metallic. It is now revealed that this element also exhibit superconductivity. Two metallic phases, formed at 93 and 160 gigapascal demonstrate transition to the superconducting state at temperatures of 10 and 17 K respectively, the highest yet seen in a solid element.

Nature, 27 Nov., 1997

Academy News

A Golden Jubilee of Indian Independence Series Lecture was delivered by Dr. S.M. Lee, Indira Gandhi Centre for Atomic Research, Kalpakkam, on "Significance of the Fast Breeder Reactor Programme" on Saturday March 21, 1998, at Mehta Research Institute, Jhusi, Allahabad under the joint auspices of the *National Academy of Sciences, India* and *Mehta Research Institute, Allahabad.*

Dr. S.M. Lee explained the significance of the developments in Fast Breeder Reactor (FBR) technology for providing long term energy security in India. Installed electric capacity in the country has increased from about 2 GWe in 1950 to over 85 GWe at present. It is projected that the electrical demand will not saturate till it reaches a level of 400 to 500 GWe by the first quarter of the 21st century. A study of the country's conventional energy resources indicates that even with saturation development of the hydro resources, there will be rapid depletion of the coal resurces (put at 200 billion tonnes) to sustain such an electrical demand. Development of nuclear power and utilization of India's uranium and thorium resources are essential.

For the above reasons India has developed the Pressurized Heavy Water Reactor (PHWR) system to be able to produce power from the natural uranium resources in the country. The PHWR system is now fully developed ane indigenized including fuel production, heavy water production, reactor construction and operation, spent fuel reprocessing and waste management.

India is endowed with about 60,000 tonnes of uranium and more than 3,00,000 tonnes of thorium. By means of the PHWR system our uranium resources could sustain only about 15 GWe of projected electrical demand. By developing the FBR system it becomes

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possible to use the plutonium obtained from reporcessing the spend fuel from PHWR, alongwith the unused uranium and thorium resource to grow the nuclear power capacity to the order of 400 to 500 GWe and sustain it for several centuries.

The FBR system is based on an advanced technology using liquid sodium coolant, sodium components like pumps, heat exchangers and steam generators; fuel of high plutonium content and operating at high temperatures with high fast neutron fluxes. This technology has been under development at the Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam for the last 25 years.

At IGCAR the liquid sodium cooled Fast Breeder Test Rector (FBTR) has been operating with a small experimental mixed plutonium- uranium carbide fuelled core since 1985. The reactor is operating at 12 MWt and last year produced electricity for the first time from a fast reactor in this country. The reactor is expected to be upgraded next year to the full core which will then produce 40 MWt and 13 MWe. The work at IGCAR is sustained by a chain of laboratories covering activities such as sodium component technology development, fuel and coolant chemistry, materials science, metalllurgy, post irradiation examination, fuel reprocessing, safety research, electronics and instrumentation. FBTR itself is used for irradiation testing and development of materials for the fast breeder power reactor programme.

The focus of activities at IGCAR is now the design and development work for a 500 MWe Proto Type Fast Breeder Reactor (PFBR). This reactor is expected to have its construction started towards the end of the 9th Five Year Plan and will be located at Kalpakkam. Once the commercialization of the FBR system is achieved in India a vast energy resource base will become available for the future development of the country.

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The National Academy of Sciences, India

5, LAJPATRAI ROAD, ALLAHABAD - 211 002

SICO-Sponsored The National Academy of Sciences, India Award 1998

The National Academy of Sciences, India invites nominations from Presidents of approved Scientific Societies of all-India character; Vice-Chancellors/Directors/ Deans of Faculties of Sciences, Technology etc. of Universities, I.I.Ts, Engineering Institutions and Colleges etc. and recognised Research Institutes; Directors of National Laboratories; Chairmen of Atomic Energy, Space, Oil and Natural Gas and University Grants Commission; Members of the Planning Commission; Secretaries of various Departments concerned with promotion of Science and Technology in any form at the Centre or in the States; Managing Director, The Scientific Instrument Co. Ltd., Allahabad; Members of the Council of the National Academy of Sciences, India, Allahabad. for the SICO-sponsored The National Academy of Sciences, India Award (1998) in the area of Instrumentation.

Nominees should be Indian citizens who have made original contributions in any field of Instrumentation. There is no age limit for nominees but the Award would be made mainly on the basis of work done in India, specially during the last 5 years.

General Regulations and Proforma of nomination form are reproduced below.

Nominations complete in all respects should reach the General Secretary, The National Academy of Sciences, India, 5, Lajpatrai Road, Allahabad - 211 002 latest by August 14, 1998.

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The National Academy of Sciences, India

5, Lajpatrai Road, Allahabad - 211002

SICO-Sponsored The National Academy of Sciences, India Award - 1998

GENERAL REGULATIONS

Preamble

1. The Scientific Instrument Co. Ltd., Allahabad, celebrated their platinum jubilee in 1986. As a part of their celebration activities, the Scientific Instrument Co. Ltd. sponsored through the National Academy of Sciences, India awards named SICO-sponsored The National Academy of Sciences, India Award. The award is to be given every third year. In 1986, 1989 and 1992 the awards were made in the fields of Instrumentation, Biotechnology and Environmental Sciences and in 1995 the award was made in the area of Instrumentation only.

   The fifth award in the series in the area of Instrumentation is proposed to be given in 1998.

2. **Details of Award**

   (a) The award will be given in the area of Instrumentation.

   (b) *Value of Award*

   The Award will carry a sum of Rs.10,000/- (Rupees Ten thousand only) in cash and a Citation highlighting the main scientific contributions of the awardee.

   Eligibility

   Any Indian citizen engaged in scientific work in the aforesaid area in India may be nominated for the Award in the proforma (See Annexure).

   Nominee will be adjudged mainly on the basis of his/her work done in an Indian Institute/Laboratory. Nominee working in India would not be considered for Award on the basis of the work done abroad. Research work during the last 5 years will form the main basis for selection. New discoveries/inventions, particularly by young and up-coming scientists would be given high consideration. There will be no age limit.

3. **Procedure for nominations**

   Nominations for the SICO-Sponsored The National Academy of Sciences, India Award may be made by the following -

   (i) Presidents of approved Scientific Societies of all-India character.

   (ii) Vice-Chancellors/Directors/Deans of Faculties of Sciences, Technology etc. of Universities, I.I.Ts, Engineering Institutions and Colleges etc. and recognised Research Institutes.

   (iii) Directors of National Laboratories.

   (iv) Chairmen of Atomic Energy, Space, Oil and Natural Gas and University Grants Commission.

   (v) Members of the Planning Commission.

   (vi) Secretaries of various Departments concerned with promotion of Science and Technology in any form at the Centre or in the States.

   (vii) Managing Director, The Scientific Instrument Co. Ltd., Allahabad.

   (viii) Members of the Council of the National Academy of Sciences, India, Allahabad.

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4. **How to make nominations**

Nominations may be made as per proforma given in the Annexure. Ten copies of the completed nomination form should be sent to the General Secretary, The National Academy of Sciences, India, 5, Lajpatrai Road, Allahabad-211 002 alongwith one set of research papers, technical reports/reports pertaining to R&D work and other documentary evidence of the significant contributions of the nominee. The nominations should be signed by the sponsors and should be sent in a sealed envelope marked 'SICO-SPONSORED NASI AWARD'.

5. **Last date for receipt of nominations**

Nominations duly completed for Award for 1998 must be received in the office of the Academy latest by August 14, 1998.

Note: Nominations received for 1995 would not be considered for award for 1998.

Selection of Awardee

Nominations will be screened by Expert Committee and a final selection will be made by the Council of the Academy, whose decision shall be final.

Presentation of Award

The Award for 1998 will be presented at a function to be held during the Annual Session of the Academy at Lucknow from October 23-25, 1998. The Academy will bear the cost of travel and accommodation of the awardee. Awardee will be expected to deliver a talk of his/her major contributions at the time of award ceremony.

Instructions for Sponsors

1. The form should be completed in all respects and ten copies, duly signed, should be forwarded to the Academy.
2. Nominations should be sent in a sealed envelope marked **'SICO-Sponsored NASI Award"** addressed to the General Secretary, The National Academy of Sciences, India, 5, Lajpatrai Road, Allahabad - 211 002.
3. Nominations which are incomplete in any respect shall not be considered.
4. The Bio-data of the nominee should accompany the nomination form. Research papers published by the nominee should be arranged in a list giving, names of the journals, volumes, number and section, if any, and page numbers. Significant research papers concerned with the Award should be specially indicated by an asterisk (*) in the list. Technical reports and other such publications should be separately listed.
5. At least one reprint/photocopy of the significant research papers/technical reports and other such publications should accompany the nomination.
6. The sponsors would also provide a write-up (in about 500 words) regarding nominee's
   (a) Significant contributions in the area of Award,
   (b) Impact of the work of the nominee on national development in the area,
   (c) Mention of places where R&D work has been utilised (Supported with relevant documents).
7. Details of patents taken by the nominee, if any.
8. Names and addresses of 3 experts in the area.

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ANNEXURE

SICO-Sponsored The National Academy of Sciences, India Award

Nomination Form

1. Area for which the nomination is to be considered:

INSTRUMENTATION

2. Bio-data of the nominee
   (a) Name
   (in block letters)
   (b) Date and place of birth
   (c) Present position and address
   (d) Position held in chronological order

Designation *Period* *Institution/Organisation*

   (e) Academic qualifications
   (beginning with Bachelor's degree)
   (f) Other Awards/Honours received

Name of Award/Honour *Sponsored by* *Year of Award*

   (g) Details of association with academic bodies
   including Fellowship etc.

3. Research contributions of the nominee
   (a) List of Publications*. (At least one reprint/photocopy of the significant research papers/ technical reports and other such publications should be enclosed).
   (b) Significant contributions in the area in which the nominee is nominated for the Award, specially during the five years preceeding the nomination.
   (c) Books/monographs/memoirs.
   (d) Patents, Recognitions obtained.
   (e) Brief account (in approximately 500 words) of the main contributions of the nominee which, in the opinion of the sponsor, should form the basis of his/her selection.
4. Write up on the impact of the work of the nominee on national development in the area. Please also mention the places where R&D work has been utilized (Supported with relevant documents).
5. Names and addresses of 3 experts in the area.

Sponsor's signature

Sponsor's Name :
Designation & Address :
Date :

---

* Research papers published by the nominee should be arranged in a list giving names of the journals, volumes, number and section, if any, and page numbers. Significant research papers concerned with the Award should be specially indicated by an asterisk (*) in the list. Technical reports and other such publications should be separately listed.

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From the very nature of such publication, it is imperative that the authors are as brief and precise in presenting their work as possible. The following restrictions will be imposed :

(a) Each communication may not contain more than 1500 words. It should be preceded by an Abstract of not more than 50 words and subject classification.

(b) Manuscripts should be typewritten in English, double spaced and should be submitted in triplicate. All mathematical expressions should be typed or written clearly in black ink.

(c) The communication should contain a minimum number of tables, figures and photogr. phs. Figures must be drawn in such a way that they can be reduced to one column width (7.5 cm). Figures must be original drawings or exceptionally sharp gloss' prints of about manuscript size. The space occupied by the figures/tables/photographs will be at the expense of text, because no LETTER which occupies a space more than 1500 words space may be published.

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Author Year Journal vol. beginning page

White, M.J.D. (1973) Animal Cytology and Evolution, 3rd Ed., Cambridge University Press, London, p. 320 (For Books).

Osgood, C. F. (1977) in Number Theory and Algebra, ed. Zassenhaus, H., Academic Press, New York, p. 321 (For edited Books).

Abbreviations of the names of periodicals should conform to those given in the World List of Scientific Periodicals.

(e) Key words : A maximum of 5 key words should be supplied. Each of these words will be separated by a slash (/) and printed just below the title of the research paper, e.g. (steroid receptors/protein-DNA interactions/gene regulation).

(f) Acknowledgments, if any, should appear at the end of the letter, but just before the references.

(g) Proofs will not ordinarily be sent to authors. If more than 100 reprints are needed, indicate the extra number while sending the manuscript.

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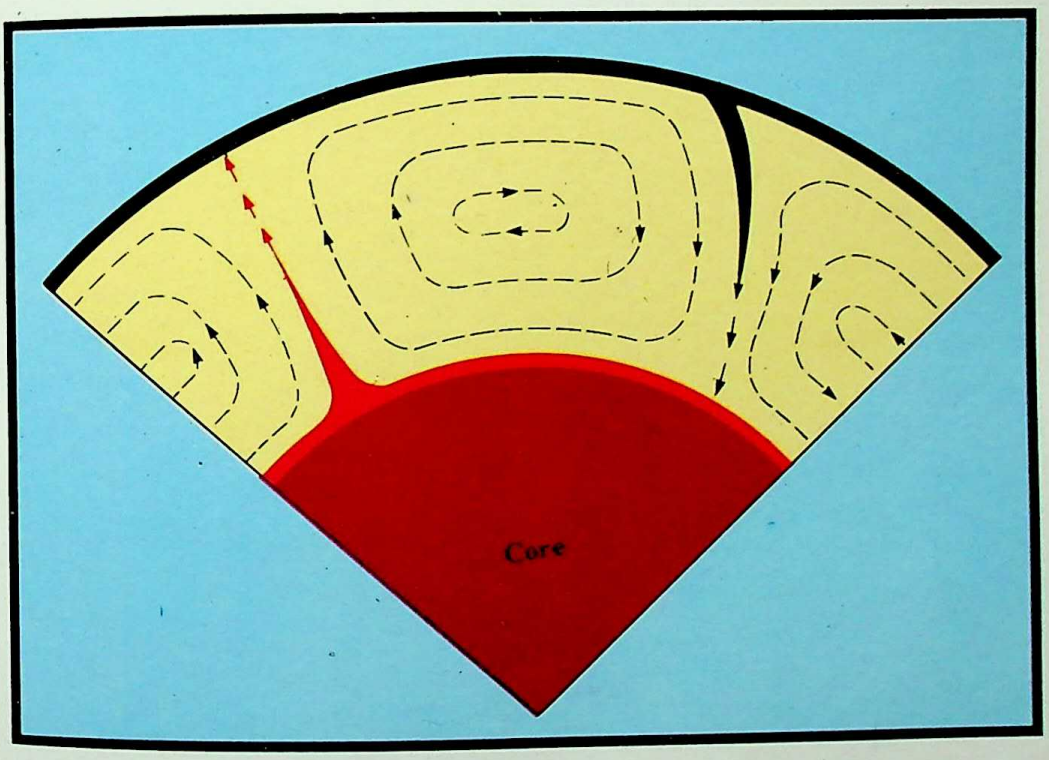

A Monthly Journal of Research

NATIONAL ACADEMY OF SCIENCES, INDIA

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The Journal publishes short communications containing original research of immediate importance. Papers containing information which break fresh grounds shall be given priority. Routine investigations which report merely experimental observations or routine modifications in theory are not usually accepted.

Occasional articles on scientific issues of societal or national interest and news of major scientific events would be welcome.

We will also review books and monographs on scientific subjects and publish the review in this journal. The publication sent for review will be retained in the library of the Academy and one copy of the Journal in which the review is published will be sent to publisher/author free of charge.

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Foreword

Seismological studies demonstrated in the early 1950's that the solid earth has a layered structure, with at least three concentric shells :

(1) a thin outermost veneer, known as the crust (35-45 km thick below the continents and 10-15 km thick below the ocean);

(2) a rocky mantle (2890 km thick; and

(3) an iron core (3480 km in radius), the outer part of which is molten. It is generally accepted that the geomagnetic field of the earth is maintained by an electric current flowing in the outer liquid core, primarily made up of Fe-Ne alloy, which acts as an electrical conductor. It is estimated that the power needed to maintain the magnetic field is 10^9 W for a weak-field dynamo, and as much as 10^{12} W for a strong field dynamo.

Geophysical data further indicate that the rocky mantle itself can be further subdivided into possibly three layers, based on seismic velocity versus depth profile : one at a depth of 400 km ($\alpha \Leftrightarrow \gamma$ phase transformation of $[Mg, Fe]_2 SiO_4$) another at a depth of 670 km [transformation of phases predominantly with garnet–and spinal-like structure to perovskite-like structure]; and the third layer in the lower most part of the mantle (called D" layer). A. Dziewonski and his associates have developed tomographic techniques which suggest that the D" layer is laterally inhomogeneous and the core-mantle is significantly undulated, with topographic "highs" and "lows", sometimes 10 km in dimension.

Lindemann's law of fusion, developed using fundamental laws of solid state physics, provides a scientific basis for the calculation of temperature at various interfaces within the earth, on the basis of our knowledge about the elastic properties and densities of the possible mantle materials and hypothetical core compo- sition. It is established that the centre of the core has a temperature of ~ 4300° K, the inner core-outer core boundary a temperature of 2850°K, and the crust- mantle boundary (Mohorovicic discontinuity) is at 550°K.

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The earth is losing heat at the rate of 42 tetrawatts (10^{12} watts) per year. It is estimated that about eight terrawatts is due to radioactive decay within the crust, while another 34 tetrawatts are lost from deeper sources in the mantle (21 tetrawatts), secular cooling (10 tetrawatts) and at least 3 tetrawatts, of heat by the core (at least 10% of the total heat flux from the interior of the earth). The heat source inside the core is contributed by secular cooling and release of latent heat, and gravitational energy released due to cooling of the core.

Because of difference in temperature between the outer shell and the inner core, convective cycles occur inside the earth, a reality conceived as far back as in 1881 by Osmoned Fisher and by Arthur Holmes in 1931. The convection at the core and overlying mantle may result in frictional and magnetic coupling. Frictional coupling would be related to viscous stress associated with the velocity shear at the top of the core. The value of the couple (< 0.1 HU) may be too small. There may be magnetic coupling as well. Although the source of the electric current is probably confined primarily to the core, there may be leakage of currents from the core to the D" layer in the mantle. The current may be induced because of changing hydromagnetic states of the core. The thermal coupling of the mantle to the core is significant in determining the dynamic state of the core. Heat loss results from mantle convection, which ultimately drives the lithospheric slabs. The heat from the core is considered to be lost by ascent of plumes through the mantle.

Different models have been suggested in relation to the convective cycles inside the mantle. They may be grouped into two categories :

(1) those involving whole mantle convections; and

(2) those involving two-layered mantle convection.

According to the two-layered convective model, the 670 km discontinuity marks an interface between the two convective systems. In this model the peridotitic rocks, which predominate the upper mantle are believed to be depleted chemical differentiation and growth of the crust. Occasional transfer of materials between the two layers occur. The other model involves ascent of mantle materials from the core-mantle boundary to the mid-oceanic ridges and subduction of the lithospheric materials right up to the core:

In the ocean basins, there are ridge systems (1-3 km) above the ocean floors with a total length of more than 60,000 km. The ridge systems are the places where new oceanic lithospheric materials are generated. The piles of lavas that are extruded along the ridges are polarized magnetically, according to prevalent polarity direction of the earth's dipole. The lava piles are pushed away from the ridge at the rate of 1 to 10 cm per year. Hot mantle materials ascend along adiabates below the spreading centre. After a few million years, the lithosphere moves away, and another set of magmatic eruptions takes place along the ridge systems. The ferromagnetic minerals within the new set of lavas assume new polarity directions as they cool below the Curie temperature. The direction of magnetization record polarity reversal of the earth's dipole magmatic

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axis. Pile of magmas are thus noted on either side of the ridge systems, showing alternate normal reverse polarity. This keeps a record of lithospheric movements. The lithosphere subducts at the end of its long journey from the ridge systems along the trenches as a part of descending mantle cycle. As the cold subducted slab descends, it gets heated. Metasomatism and metamorphism occurs in the overlying astheno sphere. Finally melting of the subducting slab generates a new set of magmatism in the continental margins. The ridges and continental margins i.e. the places of ascent and descent of the convicting cycles of the mantle are the places of intense seismic activities.

Volcanism associated with continental rift system, collision zones of two plates or interpolate volcanism, (connected with the rise of hot plumes from the core-mantle boundary), are all manifestations of mantle convective cycles.

The dynamic earth, which has been evolving as a part of the cooling process and convection, was the subject of an intence scientific discussion in a symposium organized by the National Academy of Sciences (India), in which apart from leading Indian earth scientists, several distinguished geologists and seismologists from abroad participated.

The papers presented in the symposium covered different aspects of this interesting and important subject. The present volume which incorporates these papers, should hopefully provide excellent material to understand different aspects of this evolving subject, in the light of current information, and possibly help to synthesize them in a coherent form.

I sincerely hope that the volume would not only be found useful by established researchers but also would serve as a source of information and inspiration to the upcoming generation of earth scientists.

PROF. M. G. K. MENON
F. R. S

M. N. Saha Distinguished Fellolw
of
The National Academy of Sciences, India
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Preface

There seems to be a consensus amongst cosmologists that like all other terrestrial planets, the Earth evolved by accretions of planetesimals in the solar nebula. The evolution took place in several stages. It is also believed that the earth went through a major melting process causing the generation of magma ocean and the cooling process of the molten liquid resulted in density stratification. This led to formation of different seismological and petrological discontinuities in the mantle.

The earth has an iron core (radius : 3480 km), an essentially a rocky mantle (2890 km thick) and a thin crust, formed by extrusion of materials from the mantle. There is a large temperature difference between the centre of the earth (4,300 k) and the crust-mantle interface (540 k). This drives the heat engine within the earth. Gradual loss of heat causes convective cycles involving the mantle and the core. The convective cycles in turn, cause plate motion at a rate of 5 to 10 cm per year. The core likewise is cooled by plumes that rise from the base of the mantle to the suface of the earth forming hot spots, resulting in extensive volcanism in the form of flood basalts.

The mode of convective cycles as visualized by various scientists is different. There are geophysicists, who believe in the whole mantle convection, whereas there are others who suggest layered mantle convection. Volcanic activities in the oceanic ridges, rift valleys, different collision zones and continental margins are regions of intense volcanic and seismic activities. All these activities are surfaces manifestation of convective cycles in the mantle and core of the earth.

Our knowledge on the earth has now reached a crucial stage. On the basis of seismic tomography the stratification in the earth and thickness of different layers within it, are known with a great deal of accuracy. With the development of high pressure-temperature equipments, simulation of physico-chemical conditions within the mantle has been possible. Extensive experimental studies have eliminated a plethora of hypotheses, and a general agreement about the mineralogy and chemistry of the earth's mantle has emerged. In the next decade the earth scientists will spend a significant amount of their time in deciphering the exact nature of the convective cycles in the mantle and the core to explain the processes taking place on the surface of the earth with reasonable accuracy.

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The National Academy of Sciences (India), therefore, organized a symposium on Mantle Dynamics and its Relation to Earthquake and Volcanism. The Academy invited some of the leading earth scientists from different parts of the world. They included Prof. W. S. Fyfe (University of Western Ontario, Canada), Prof. P. J. Wyllie (California Institute of Technology, U. S. A.), Prof. K. Yagi (Hokkaido University, Japan), Prof. S. Uyeda (University of Tokyo, Japan), Prof. Dean C. Presnall (Universit of Texas at Dallas, U. S. A.) and Prof. E. G. Lidiak (University of Pittsburgh, U. S. A.). In addition, more than 100 earth scientists from different Indian geological and geophysical institutes participated in the symposium. The present special issue is an outcome of the symposium participated by different eminent scientists.

In this issue Dean C. Presnall discusses about the evolution of the earth by the process of accretion and formation of magma ocean by a giant impact with a comet. The paper also discusses about subsequent cooling process resulting in density stratification and evolution of the mantle.

A. K. Gupta describes about the presence of different seismological discontinuities within the earth, its mineralogical compositions as revealed by experimental petrological studies in different parts of the mantle and various different convective cycles within it. He further discusses about the magmatic process within the ocean ridges, rift valleys, continental margins and different seismic processes in the plate boundaries.

W. S. Fyfe writes about the cooling mechanism in the earth that leads to geochemical mixing and evolution of chemical transport system. His main discussion is on heat loss, fluid transport and geosphere-biosphere interaction in a convective planet.

P. Tiwari, U. S. Gupta and Sriniwas confine their study to determination of phase boundaries related to perturbation in basal heat flux and plume temperature. The discussion is mainly on one dimensional lithosphere thinning problem.

S. Singh, G. Kumari and K. Singh present crustal deformation model in areas of volcanic eruption. K. N. Khatri deals with the evolution of the mountain chain related to collision tectonics resulting from plate motion. His special emphasis is on seismicity related to evolution of the Himalayas. He describes in detail about a seismic hazard and risk scenario for Himalaya and Ganga plains due to a future great earthquake.

S. K. Acharya and S. Sengupta extend their study also to the Himalayas with special emphasis on the structure of Siang Window, its evolution and bearing on the nature of eastern syntaxes of this great mountain chain.

Finally S. Uyeda writes about causes of earthquakes as a result of sudden plate motion within the earth. He discusses at length about methods of short-term prediction using the VAN method developed by the Greeks. He also describes about the use of the VAN method in successfully predicting earthquakes in Japan.

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We hope that the special issue will be useful to the students and active researchers in the field of earth sciences. We have slightly deviated from the normal format of the 'National Academy Science Letters', as it was necessary to keep the originality of the presented papers.

ALOK K. GUPTA
Editor

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Crystallization of a hadean terrestrial magma ocean

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Abstract : On the basis of compositional trends of lherzolite from Kilbourne Hole, New Mexico, USA (Carter, 1970), the composition of the primitive upper mantle is calculated to have a strictly chondritic Ca/Al ratio of 1.11, a value similar to but slightly lower than values calculated by others from xenolith data. This implies that the magma ocean that produced the upper mantle crystallized at equilibrium or experienced only a small amount of fractionation a conclusion consistent with recent fluid dynamic considerations. The non-chondritic Mg/Si, Mg/Ca, and Si/Ca ratios of the mantle are attributed to volatilization that accompanied a giant impact. A working model for the Hadean history of the Earth is developed that includes (1) accretion from chondritic parental material, (2) a giant impact late in the accretion history that formed the Moon, completely melted the Earth, and caused partial devolatilization, (3) segregation of the core and mantle by gravitational separation of immiscible iron and silicate liquids, (4) crystallization of the silicate magma ocean with at most only a minor amount of fractionation, and (5) partial melting of the upper mantle through geologic time to form the continental crust and an upper mantle depleted in Si/Mg and Fe/Mg relative to the lower mantle.

(**Keywords** : planetesimal accertion/mantle evolution/ magma ocean/mantle connection)

Everything should be made as simple as possible but not simpler.

—Albert Einstein

Introduction : Current models for the origin of the Earth's mantle usually invoke crystallization of a primitive magma ocean. In order to evaluate such an origin, I first examine the basis for believing that primordial temperatures were sufficient for the existence of a magma ocean. This is followed by a discussion of fractional versus equilibrium crystallization of the magma ocean, the bulk composition and compositional variations of the present mantle, and a simplified working model for the Hadean history of the Earth.

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Accretion and Initial Melting of the Earth. The manner in which the terrestrial planets accreted has many uncertainties, but in the last 25 years a broad consensus has emerged (Safronov, 1978; Wetherill, 1976, 1985, 1990; Kaula, 1990; Dones and Tremaine, 1993a) that the terrestrial planets did not form exclusively by accertion of a large number of small objects (ordered accretion). Instead, the model generally preferred invokes stochastic accretion of planetesimals that increased in size and decreased in number with time. The modeling of Wetheril (1985) suggests that only about 10^5 years would be needed to achieve planetestimals of about 10^{26}-10^{27} g (a size range that would include objects the size of the Moon, Mercury and Mars), and that final accretion of the Earth to its present mass of 6×10^{27} g would be achieved in about 2×10^8 years. Wetherill (1985, 1990) argued that the terrestial planets experienced several large to giant impacts in the latter stages of their growth. Support for this model is provided by the spins of Earth and Mars. Dones and Tremaine (1993a, 1993b) calculated that the rapid spins of these planets could not have been produced by ordered accretion, but must have been produced instead of stochastic accretion that included one or several giant impactors.

Wetherill (1985), 1990) argued that the energy released by giant impacts is sufficient to produce partial, and perhaps even complete melting of bodies at least as small as Mercury. Because of this melting, he suggested that core formation was a process that took place simultaneously as the size of the proto-planets grew. The Moon is now generally considered to have formed toward the end of the accretionary process by collision of a very large planetesimal with the proto-Earth (Hartman and Davis, 1975; Cameron and Ward, 1976; Stevenson, 1987; Melosh, 1990). The mass of this planetesimal is commonly taken to be roughly 0.1 times that of the Earth (half the diameter of the Earth), which is about the size of Mars. Wetherill (1985) and Dones and Tremain (1993a) have suggested that the largest impactor of the Earth may have had a mass as much as three times larger than this. A collision of such a body with the proto-Earth would have an energy release several times that needed for complete melting (Wetherill, 1985, 1990). Because of the high probability of very large impacts prior to the Moon-forming event, both the proto-Earth and the giant impactor would be expected to be differentiated into a mantle and core prior to this event, and one or both of the bodies could have been at least partly molten at the time of impact. Stevenson (1987), for example, estimated that the proto-Earth could have been approximately 50% molten prior to the Moon-forming impact.

Simulations of a giant impact origin for the Moon by Benz and Cameron (1990) and Cameron and Benz (1991) yielded a completely molten Earth shortly after impact and temperatures of rock vapor at the Earth's surface of at least 16,000°K. They assumed a temperature for the proto-Earth of 4000°K immediately prior to the Moon-forming event. They make no mention of the consequences of this temperature for the physical state of the proto-Earth, but a consideration of some known melting relations is instructive. At 4000°K, $Mg_{0.88}Fe_{0.12}SiO_3$ perovskite melts at 43 GPa (Zerr and Boehler, 1993), which in the

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present Earth corresponds to a depth of about 1200 km. Perovskite is the dominant but not the only phase in the present Earth's lower mantle, and the inclusion of other components needed to make these phases would reduce the liquidus temperature of the mantle below that of perovskite alone. Thus, for the present Earth, a temperature of 4000°K would imply a magma ocean depth greater than 1200 km. For a slightly smaller proto-Earth, the magma ocean would be even deeper because pressure (and liquidus temperature) would not increase as rapidly with depth. Thus, the assumptions and conclusions of Cameron and Benz are consistent with the position of Wetherill that partial to complete melting of the proto-Earth occurred as the planet grew and that the Moon-forming impact would completely melt the Earth.

A more conservative view was expressed by Melosh (1990) and Tonks and Melosh (1993). They concluded that the amount of melting produced by the initial shock wave of a giant impact would be unlike to melt the entire Earth. For an initially hot proto-Earth (1490°K), a projectile travelling at 15 km/sec, and a projectile/planet mass ratio of 0.1 to 0.3, they found that the initial shock wave would melt 52-93% of the planet. They did not evaluate in detail the amounts of additional energy released by such processes as merger of the core of the impactor with that of the planet. Because of this, they noted that the energy associated with the initial shock wave is the minimum amount that would be available for melting. Therefore, even the conservative view of these authors allows for the possibility of complete melting by a giant impact.

Stevenson (1990) pointed out that iron liquid, at least at the low pressures existing in the upper mantle, does not wet silicates and therefore would not drain through a crystallized mantle. To overcome this difficulty, he proposed a completely liquid mantle and formation of the core by gravitational settling of immiscible iron droplets. An interesting aspect of this model, pointed out by Stevenson, is that the iron droplets (≤ about 2 cm diameter) would be small enough for chemical equilibration with the silicate mantle. This is of significance for the recent proposal (Murthy, 1991) that the abundances of siderophile elements in the mantle might be explainable by equilibration of iron and silicate immiscible liquids at very high temperature (Walker *et al.*, 1993; Hillgren *et al.* 1994). Because of the difficulty of forming the core in the absence of a liquid mantle, and because the energetics of a giant impact are favorable to or permissive of complete melting, the discussion that follows will assume that the entire mantle of the fully accreted Earth existed immediately after core segregation as a completely liquid magma ocean floating on a liquid iron core.

Fractional versus Equilibrium Crystallization of the Mantle : The only available direct samples of the mantle come from upper mantle xenoliths carried to the surface by basaltic lavas and kimberlite magmas. Conventionally, mantle xenoliths in basalts have been divided into two main groups, those that are cumulates produced by fractional crystallization of basaltic magmas (Chen *et al.* 1992), and those that are residues from varying amounts of extraction of basaltic magmas. The

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former will be ignored here. On the assumption that the latter are, in fact, residues of partial melting, plots of bulk chemical compositional trends allow the composition of the primitive unmelted lherzolite to be inferred (Carter, 1970; Jagoutz *et al.*, 1979; Ringwood, 1979; Palme and Nickel, 1985; Hart and Zindler, 1986). It is the composition of this primitive lherzolite that is of interest in the present context. Herzberg and O'Hara (1985), Takahashi (1986), Ohtani *et al.* (986), and Herzberg (1987) argued that mantle xenoliths trasitionally thought to be residues of partial fusion are, in fact, crystallized eutectic melts. However, Presnall and Gasparik (1989), Herberg *et al.* (1990), Presnall and Walter (1993), and Zhang and Herzberg (1994) showed that this model is inconsistent with high pressure phase relations of model and natural lherzolite. In the discussion that follow, the traditional view of these xenoliths as residues of partial fusion will be assumed to be correct.

Now, it may be asked if there is any chemical signature of the primitive upper mantle composition, as inferred from studies of residual mantle xenoliths, that indicates the presence or absence of fractionation of a Hadean magma ocean. To answer this question, two refractory lithophile elements, Ca and Al, may be considered that form compounds with very high condensation temperatures (1400°K). As pointed out by Ringwood (1979), refractory lithophile elements, which include Ti, Sc, and rare earth elements in addition to Ca and Al, not only would have condensed very early from the cooling solar nebula, but they would also resist volatilization during subsequent severe heating events, such as a giant impact. Abundance ratios of these elements should remain fairly constant in planetary and asteroidal materials affected only by severe heating.

However, if melted planetary materials fractionally crystallized as they cooled, compositional heterogenesis could develop, and refractory lithophile element ratios could vary depending on the relevant crystal/liquid partition coefficients.

The relative abundances of these elements in chondritic meteorites are, in fact, fairly constant, a property that is particularly well displayed by the Ca/Al ratio. Ahrens and Von Michaelis (1969) showed that the Ca/Al ratio of all classes of chondrites is remarkably constant. In a more recent compilation, Hart and Zindler (1986) found that the average Ca/Al weight ratio for all classes of chondrites is 1.09 ± 0.02. The uniformity of this ratio both for C-I chondrites, which show no evidence of melting, and for other carbonaceous chondrites, which contain chondrules crystallized from liquid, shows that the Ca/Al ratio is not affected by severe melting events. Other refractory lithophile element ratios would probably show similar levels of uniformity (Sun and Nesbitt, 1977; Jagoutz *et al.* 1979), but the Ca/Al ratio involves major elements that are reported in all analyses of mantle xenoliths.

Given that the Earth was accreted from chondritic material, the bulk silicate portion of the Earth, and therefore the bulk composition of a completely molten Hadean mantle, should have the chondritic Ca/Al ratio because :

(1) both of these elements would be largely excluded from the core, and

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(2) the Ca/Al ratio should not be affected by a giant impact that caused massive melting and volatilization.

Given an adiabatic temperature gradient in the magma ocean, it would crystallize from the bottom up; and in the case of fractional crystallization, the composition of the upper mantle would be altered by crystallization of lower mantle phases. The two phases that would crystallize in the lower mantle are Mg-perovskite and magnesiowüstite (Ohtani and Sawamoto, 1987; Ito and Takahashi, 1987; Agee, 1990; Zhang and Herzberg, 1994; Presnall *et al.,* in press) and they would be expected to crystallize in the following approximate proportions 80% perovskite, 20% magnesiowüstite (McFarlane *et al.,* 1994). Partition coefficient data for Ca and Al between Mg-perovskite and liquid have been determined by Kato *et al.* (1988a; 1988b), Drake *et al.* (1993), and McFarlane *et al.* (1994). Results from all these studies are braodly consistent. The data of McFarlane *et al.* at 24.5 GPa has been used here because of some uncertainty in the data of Kato *et al.* (Agee and walker, 1989; and Kato *et al.*, 1989) and because the data of McFarlane *et al.* are the most conservative in the sense that they imply the least extreme fractionation of the Ca/Al ratio.

On fractional crystallization of the lower mantle (two thirds of the total mantle) as a mixture of 80% perovskite, 20% magnesiowüstite, use of the distribution coefficients and procedure given by McFarlane *et al.* (1994) yields a Ca/Al ratio of 2.1 for the remaining upper mantle magma ocean. Additional crystallization of majorite in the lower part of the upper mantle (now the transition zone) would increase the Ca/Al ratio of the uppermost mantle still further (Drake *et al.*, 1993).

What, then, is the Ca/Al ratio of the primitive upper mantle by inferences from mantle xenoliths ? Ringwood considered lherzolite and as indicated basalts to be complementary and published several primitive mantle (pyrolite) compostions (Ringwood, 1975,) based on mixtures of these two components. His relatively recent pyrolite composition (Ringwood, 1979) has a Ca/Al wt. ratio of 1.27, higher than the average chondritic ratio of 1.09 but significantly lower than the value expected from crystallization of Mg-perovskite, magnesiowüstite, and majorite. Jagoutz *et al.* (1997) selected five primitive lherzolite xenoliths high in Ca and Al and located close to the intersection of the ordinary chondrite and xenolith fractionation trends on a Mg/Si *vs* Al/Si plot. The average of these five xenoliths gave a Ca/Al ratio of 1.19. Palme and Nickel (1985) fitted trend lines to plots of the concentration of various oxides and elements *versus* MgO concentration. They chose values at 35.5% MgO as their primitive mantle composition, which yielded a Ca/Al ratio of 1.24. A common feature of all these studies is a Ca/Al ratio somewhat higher than the chondritic value.

Hart and Zindler (1986) followed the procedure of Jagoutz *et al.* (1979) by choosing, as their primitive upper mantle composition, the intersection of the xenolith and ordinary chondrite trends on a Mg/Si *vs* Al/Si plot. However, they were dissatisfied with the resulting high Ca/Al ratio, and postulated that

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this was caused by the tendency of geologists to select pretty xenoliths enriched in emerald-green diopside. They arbitrarily reduced the amount of model diopside in their samples to obtain the chondritic Ca/Al ratio of 1.09. Although the suggestion by Hart and Zindler of sampling bias seems plausible, reduction of the amount of diopside just enough to achieve the chondritic Ca/Al ratio interjects an undesirable modeling bias. The early study of spinel lherzolite xenoliths from Kilbourne Hole, New Mexico, USA, by Carter (1970) addresses this issue directly. Carter collected the samples before the locality generally known to mineral collectors, so the xenolith population as found, was essentially as erupted (J.L.Carter, personal communication). Also, all the xenoliths studied by Carter were randomly selected in the field prior to examination of their mineralogy. No bias toward samples rich in diopside could have occurred because all the xenoliths were covered with a skin of basalt. Unfortunately, the chemical data reported contain an error in the Al_2O_3 values (J. L. Carter, personal communication). For xenoliths with an olivine composition of Fo_{88}, Carter found, subsequent to publication of his 1970 paper, that the correct Al_2O_3 content should be 0.8 times the value reported. Also, because SiO_2 was not analyzed and was determined by difference, the corresponding SiO_2 values should be increased by the same amount as the Al_2O_3 is reduced. When these corrections are made, the anomalies in the Al_2O_3 (too high) and SiO_2 (too low) concentrations simultaneously disappear. In a modern study, an electron microprobe would be used for the mineral analyses, but when bulk analyses of minerals are desired, atomic absorption and colorimetry, the methods used by Carter on carefully hand-picked mineral separates, would actually be superior. The only deficiency is the lack of direct analytical data for SiO_2, but since all other major elements were analyzed, this is not a serious objection as long as the values for all the other elements are accurate.

Carter (1970) determined average values for xenolith bulk compositions *versus* fayalite content of the olivine. An approximate correction of these average compositions were made, by reducing Al_2O_3 to 0.8 times the given value regardless of fayalite content and increasing SiO_2 by an amount equal to the lost Al_2O_3. When these averages are plotted on a Mg/Si *vs* Ca/Si or Mg/Si *vs* Al/Si plot along with the chondritic trends, the intersection gives a primitive mantle composition with a forsterite content in olivine of $Fo_{88.6}$ and a Ca/Al ratio of 1.11, essentially the chondritic ratio. The true corrections to the values of Al_2O_3 and SiO_2 reported by Carter (1970) would vary somewhat depending on fayalite content of the olivine. However, this is of little importance in the present context because of the fortuitous circumstance that the chondritic and xenolith trends interest at $Fo_{88.6}$, extremely close to the forsterite content at which the correction has been determined. Table 1 gives the concentrations of some of the most important oxides for the primitive upper mantle composition at $Fo_{88.6}$. Note that $Fo_{88.6}$ corresponds to Mg/(Mg + Fe) in the bulk composition of 0.884. This is mainly because a small amount of iron is contained in spinel. The primitive Ca/Al ratio of 1.11 would seem to support the contention of Hart and Zindler (1986) that sampling bias exists in other

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Table 1 – Primitive upper mantle compositions.

	SiO_2	Al_2O_3	MgO	CaO	Mg/(Mg+Fe) (atomic)	Ca/Al (weight)
Ringwood (1979)	45.1	3.3	38.1	3.1	0.90	1.27
Jagoutz *et al.* (1979)	45.2	3.97	38.3	3.50	0.90	1.19
Palme & Nickel (1985)	46.2	4.75	35.5	4.36	0.89	1.24
Hart & Zindler (1986)	46.0	4.06	37.8	3.27	0.90	1.09
This study	44.0	4.07	38.4	3.34	0.884	1.11

studies. However, Ca/Al for Kilbourne Hole xenoliths increases with the forsterite content of olivine and has the value 1.21 at Fo_{90}, which is the commonly assumed forsterite content of olivine in the primitive upper mantle. In the present analysis, the forsterite content of olivine ($Fo_{88.6}$) in the primitive upper mantle is obtained directly from the Mg/Si *versus* Ca/Si plot. This derived value, which is consistent with a composition of Fo_{86-88} obtained on independent grounds by Carter (1970), is considered to be more soundly based than the commonly assumed value of Fo_{90}.

To extend the results at Kilbourne Hole to the entire upper mantle is, of course, a very large extrapolation; but it should be noted that data from other localities have not been analyzed by the same procedures as those used by Carter. If the result from Kilbourne Hole is indeed generally applicable, one must conclude that the primitive upper mantle, exclusive of volatile elements, is un- fractionated (± 2%) relative to chondrites. However, even if the Ca/Al values found in other xenolith studies are used (Table 1), the amount of fractionation would be small. This conclusion is consistent with those of Kato *et al.* (1988a; 1988b) and Drake *et al.* (1993) based on partitioning of a number of refractory lithophile elements in addition to Ca and Al. If the Earth accreted from chondriti material and a global magma ocean existed, this implies either (1) minor to no fractionation during crystallization or (2) elimination of chemical heterogeneities produced during crystallization (Ohtani, 1985; Agee and Walker, 1988; Miller *et al,* 1991) by subsequent convective mixing of the crystallized mantle.

Tonks and Melosh (1990) noted that convection in a deep magma ocean would be sufficient by turbulent and vigorous that crystals up to about 0.5 cm in diameter would remain suspended in the magma would not settle out. Further, they calculated that the upward percolation speed of interstitial melt from the lower crystallizing layer would be much smaller than the speed of advancement of the 50% crystallization surface. Therefore, leakage of interstitial melt back into the main body of magma would not occur, and the magma ocean would crystallize without

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fractionating. They noted that as the magma ocean approaches complete solidification, the rate of advance of the crystallization surface would decrease due to less intense turbulence and reduced heat loss, so that some leakage of interstitial melt may occur in the upper 100-200 km. Whereas Tonks and Melosh (1990) considered melt fractions greater than 0.5 in the basal crystal/liquid layer, Solomatov and Stevenson (1993) focused on the behavior of smaller melt fractions. They concluded that the lower mantle and possibly a major fraction of the upper mantle would be completely unfractionated and that fractionation by percolation of melt from the upwardly advancing crystal/liquid layer would be important only in the upper 150 to 300 km. Thus, their conclusions were essentially the same as those of Tonks and Melosh (1990). The fluid dynamic behavior of this process is not yet completely understood, but appears to be supportive of geochemical models that avoid fractionation except possibly in the late stage of solidification.

Present State of the Mantle and a Model for the Hadean History of the Earth : As emphasized by Hart and Zindler (1986), the primitive upper mantle, when compared to C-1 chondrites is depleted in both Mg and Si relative to refractory lithophile elements such as Ca and Al. For example, C-l chondrites have Mg/Ca and Si/Ca wt. ratios of 11.4 and 12.3, respectively (Anders and Grevesse, 1989), whereas in the primitive upper mantle composition determined here, these ratios are 10.5 (8% depletion) and 9.4 (23% depletion), respectively. The primitive upper mantle composition deduced by Hart and Zindler shows similar depletion percentages. Therefore, if the composition of the primitive upper mantle is representative of the whole mantle, as argued above, then the composition of C-l chondrites cannot match the bulk composition of the Earth. This problem has been extensively discussed by many authors (Hart and Zindler, 1986).

It is well known that the Earth is depleted in volatile elements to those in C-l chondrites. If the accretion history of the Earth includes one or more giant impacts, as favored here, a necessary consequence is extensive volatilization (Cameron & Benz, 1991; Tonks & Melosh, 1993). Both Mg and Si are slightly volatile relative to the strictly refractory lithophile elements, and Si is slightly more volatie than Mg (Ringwood, 1979). Thus, as pointed out by Hart and Zinder (1986), one or more giant impacts would be expected to cause modest depletion of both Mg and Si, and greater depletion of Si than Mg, exactly as observed. By this model, the Earth is accreted from chondritic material, abundance ratios of refractory lithophile elements in the Earth are inherited from the chondritic parent material, and slightly to highly volatile elements (including Mg and Si) show varying degrees of depletion. Thus, the abundances of both volatile and refractory elements in the Earth are readily understood as natural consequence of expected processes, and no *ad hoc* explanations are needed.

On the basis of thermoelastic data, it has been argued that the lower mantle is enriched in Si/Mg and Fe/Mg, or both, relative to the upper mantle (Knittle *et al.* 1986; Jeanloz and Knittle 1989; Stixrude *et al.* 1992; Hemley *et al.* 1992; Ita and Stixrude, 1993), although this

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has been disputed (Wang *et al.* 1991; Weidner and Zhao, 1992; Wang and Weidner, 1994; Wang *et al.* 1994). The primitive mantle probably no longer exists beneath any of the present crust. Average compositions of residual mantle xenoliths typically found in basaltic eruptions are somewhat more depleted (lower in Si/Mg and Fe/Mg) than the primitive mantle composition calculated here; and it is reasonable to relate this depletion to formation, through time, of the overlying crust by partial melting. Thus, the present upper mantle would be expected to have exactly the same compositional difference from that of the lower mantle as some have inferred from thermo-elastic data.

The working model proposed here for the Hadean history of the Earth involves :

1. accretion from chondritic material,

2. a giant Moon-forming impact to melt and partially devolatilize the Earth,

3. gravitational separation of immiscible iron and silicate liquids to form the core and mantle,

4. equilibrium crystallization of the mantle from the bottom up with either no fractionation or fractionation only in the upper 150-300 km, and

5. partial melting of the upper mantle to form oceanic and continental crust and a complementary residual upper depleted in Si/Mg and Fe/Mg and relative to the deep mantle.

This model is similar than other proposals that employ various scenarios for fractionation of the magma ocean to produce a compositionally layered mantle. However, there are no data for the present mantle that demand this initial heterogeniety. Therefore, until a more complex model is required, the simple one presented here is preferred.

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Evolution of the mantle :the convective cycles and their relation to earthquake and volcanism

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Abstract : It is generally accepted that the earth was formed in the solar nebula by accretion of planetesimals of composition similar to a carbonaceous chondrite. In the early stage, the proto-earth was of small size, but in different stages of grwoth process the mass of the nucleus of the earth gradually increased. The moon might have been formed due to collapse of a sediment ring formed toward the end of its growth process. Other hypothesis suggests that the moon might have been formed toward the end of the accretionary process by collision between a very large planetesimal with the primitive earth. A part of the planetesimal was thrown off in space forming moon, whereas the remaining part accreted with the earth. The impact caused increase the temperature of the earth leading toward melting of a significant part of the earth's interior forming a magma ocean. The process of core formation involving sinking of a huge droplet of Fe-Ni alloy in a magma ocean was probably fast.

Experimental studies at high pressure indicate that at and above 25.5 GPa fractionation of (Mg, Fe) SiO_3 perovskite and addition of olivine in a chondritic magma ocean can produce a relatively Fe-free, Mg-rich peridotitic upper mantle. At these pressures olivine will float at the top, whereas denser liquid should sink.

Because of difference in heat between the core and the surface of the earth there are convective cycles inside the earth. According to some suggestions, there are convections involving the whole mantle right from the outer core of the earth. The other hypotheses suggest two-layered convection with occasional transfer of material between the two layers. Upwelling of hot mantle material takes place in the mid-oceanic ridges and continental rift zones. New oceanic crust (15 km^3 of magma is produced along the ridges) so generated along the ridges move away for thousands of miles before subducting along the continental margin. Subducted oceanic lithosphere, which are marked by earthquake foci is a physically defined part of mantle convection. Partial melting of the subducted materials produces volcanism in the continental margin. Collision zones between two oceanic or two continental plates are also sites of volcanism and earthquakes; all these seismic and volcanic activities are surface manifestation of energy distribution through mantle convection.

(**Keywords** : *man*tle evolution dynamics)

Introduction : Cosmologists believe in general that evolution of terrestrial planets took place by accretion of planetesimals in a solar nebula. Carbonaceous chondrites (type-1) are dominant undifferentiated objects in the asteroid belt, and they have approximately the solar abundance of non volatile sediments (Andre and Gravasse, 1989). Chondrite may therefore, represent the primitive dust particles in the solar nebula (Urey, 1953, Chapman, 1976). Ringwood (1975) believed that the

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process of accretion took place in different stages.

In the early stage of accretion, the energy involved was small and the process of accretion was slow, but in each successive stage the nucleus of the earth was increased. This was followed by increase in the energy of impact of the planetesimals.

The model of Wetherill (1985) suggests that only about 10^5 years would be needed for the growth of an object having a size of about 10^{26}– 10^{27}g (a size range equivalent to that of the size of the Moon, Mercury, and Mars), and the final accretion of Earth to its present mass of 6– 10^{27}g would be achieved in about 2– 10^8 years. Wetherill (1985, 1990) argued that the terrestrial planets experienced several large to giant impacts in the later stages of their growth. Support for this model is provided by the spins of the Earth and Mars. According to Presnall (1994), calculation of Dones and Tremaine (1993a, 1993b) show that the rapid spins of these planets could not have been produced by ordered accretion, but were due to stochastic accretion that included one or several giant impacts. The energy released by giant impacts is sufficient to produce partial, and perhaps even complete melting of bodies at least as small as that of Mercury. Because of this melting, he suggested that core formation was a process that took place simultaneously as the size of the proto-planet grew. The moon is now generally considered to have been formed toward the end of the accretionary process by collision of a very large planetesimal with the proto-earth (Hartman and Davis, 1975; Cameron and Benz, 1991; Stevenson, 1987; Melosh, 1990), Stevenson (1987), for example, estimated that the proto-earth could have been approximately 50% molten prior to the moon-forming impact. Ringwood (1975) however, believe that the formation of moon is related to the collapse of a sediment ring, which once encircled the earth. This ring was believed to have been formed toward the later stage of the growth process of the protoearth. Thus the suggestion of Wetherill related to the formation of moon is quite different from that of Ringwood (1975).

It is well known that the Earth is depleted in volatile elements relative to those in C-l chondrites. If the accretion history of the Earth includes one or more giant impacts, a necessary consequence is extensive volatilization (Cammeron and Benz, 1991; Tonks and Melosh, 1993). Both Mg and Si are slightly volatile relative to the strictly refractory lithophile elements, and Si is slightly more volatile than Mg (Ringwood, 1979). Thus, one or more giant impacts would be expected to cause more depletion of both Mg and Si, and greater depletion of Si than Mg, exactly as observed.

Layered Structure within the Earth with Special Reference to Mantle : Whereas there is controversy regarding the evolution of the terrestrial planets, there is a general consensus that significant portion of the mantle was molten at certain stage of its evolution, and there was density stratification within it forming different layers.

Seismological studies indicate that the earth has a layered structure. The top layer called the crust is composed of loose sediments near the surface followed by sedimentary rocks, granitoid and finally granulites at the

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bottom of the crust. It is 35 to 45 km thick below the continents but 10 to 15 km thick in the oceanic region. The mantle is extended below the crust to a depth of 2850 km, below which lies the core of the earth, which has two segments : the upper part (3000 km thick) is considered to be in liquid state, whereas the inner core (2000 km thick) is present in a solid state. It is generally believed that the core of the earth is made up of an iron-nickel) alloy. It has been observed that the bulk modulus of pure iron is larger than that of the core. It has also been estimated by the geophysicists that the density of pure liquid iron is 10% larger than the density of the core. This suggests presence of lighter components associated with iron (like a small percentage of Ni). According to Melchior (1986), the number of candidates may be restricted to three : silicon, sulfur and oxygen.

The present discussion is related to the variable mineralogical composition of the mantle causing seisomological heterogeneity, its evolution and convective cycles. These different aspects are discussed below.

Heterogeneity in the Mantle : The mantle is fairly heterogeneous with several seismological discontinuities. Nolet *et al.* (1994) gave an overview of recent seismological evidence on heterogeneity in the upper mantle. Figs. 1 (a) and 1 (b) of Nolet *et al.* demonstrates variation in P- and S-wave velocity propagation (long period or broad-band observation) or as a function of depth; this shows presence of heterogeneity in mantle structure. Early surface wave studies (Knopoff, 1972; and Kovach, 1979) established the presence of a low shear velocity zone or LVZ between 150 and 200 km. A common feature of both short and long period refraction study showed that there is a relatively high gradient within the transition zone from 410 to 660 km depth. They observed that the overall increase in velocity from about 425 to 625 km is well-resolved. The details of velocity-depth gradient within the mantle are uncertain. Some geophysicists consider the existence of a second order dicontinuity also at about 520 km depth (Mechie *et al.* 1993); this according to Nolet et al. is not well-established. Some regional models have a high gradient zone near this depth having lower slope above and below. On the basis of his observations of stacked phases originating at this depth, Schearer (1990) recently discussed on the existence of phase transformation in this zone.

The discontinuity at 660 km, which separates upper mantle from the lower mantle is a good reflector with near vertical, 1-Hz P-waves, showing that the transition zone has a width of 4km or less. This supports the idea that this discontinuity is sharp (Vinnik, 1977).

The 400 km discontinuity is a poorer reflector and spread over more than 5 km depth. In some regions, the 400 km discontinuity reflect short period waves. There have been description of some secondary doscontinuities, which are however, not well constrained. Revenaugh and Jordan (1991) reported S-H wave discontinuity at a depth of 300 km beneath the shield region of western Australia and 200 km below northern Australia. At these depths, a velocity jump has been noted.

Grand (1994) produced maps of lateral variation in shear velocity wighin the mantle

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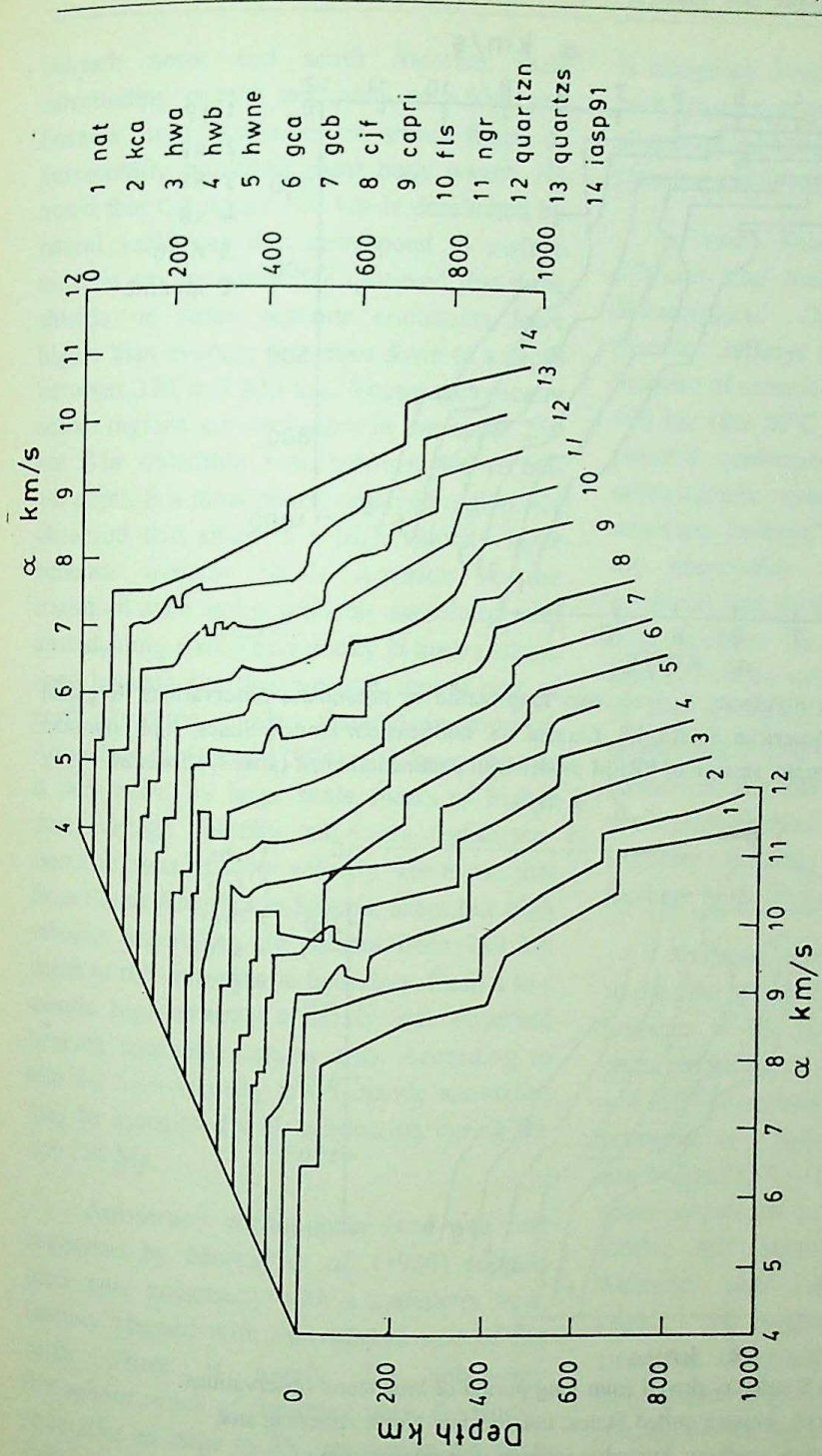

Fig. 1 (a)–Upper mantle models derived from short-period P- observations, show a considerable variation in structure. The upper mantle structure of iasp 91 (Kennett and Engdahi, 1991) was designed to provide a reasonable average of continental structure. Regional coverage : nat, North Atlantic, hwb, hwa, hwne, west- central United States : gca, gcb, cjf, western North America; capri, fls, ngr, northern Australia, quartzn, quartzs, Asiatic Russia. Upper mantle models derived from short-period P-waves observations show a considerable variation in structure (after Nollet et al. 1994).

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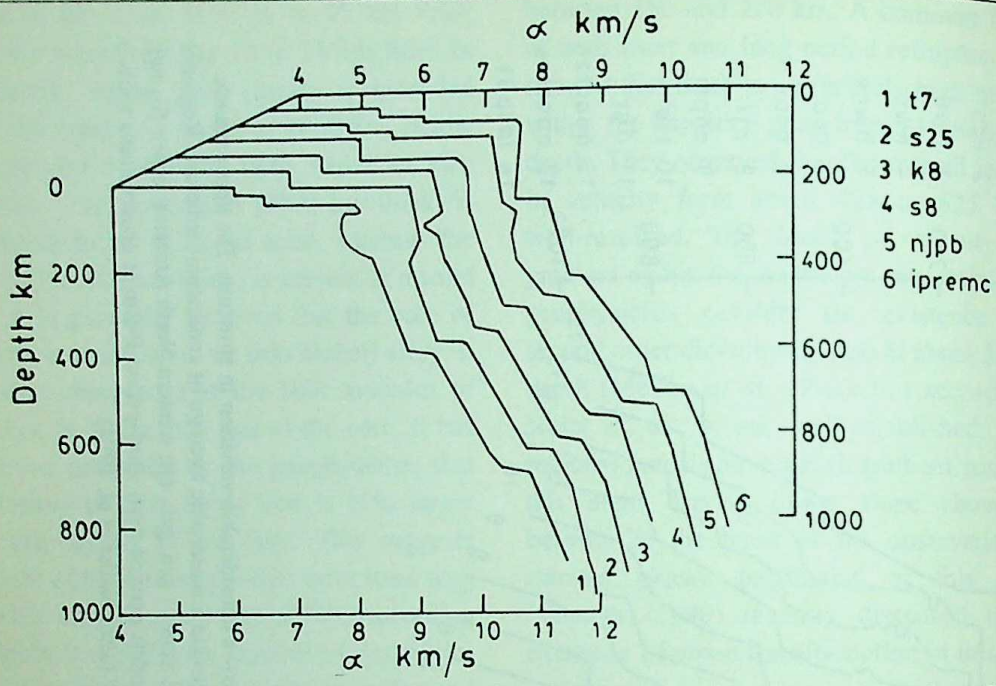
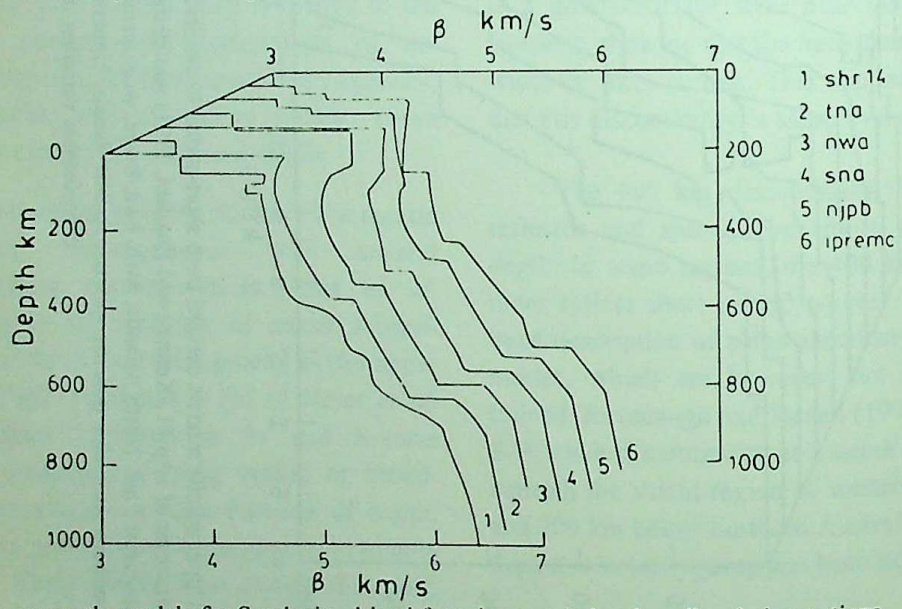


1(b)–Upper mantle models for P-velocity derived from long-period or broadband observations. Regional coverage : s25, North American Shield; k8, Eurasia, s8, northeastern United States; njpb, northern Australia; impremc, Isotropic version of PREM model with continental crust (after Nollet *et al.* 1994).



1(c)–Upper mantle models for S velocity drived from long-period or broadband observations. Regional coverage : shr14, western united States; tna, tectonic North America; sna, shield North America; njpb, northern Australia; ipremc, isotropic version of PREM model with continental crust (after Nollet *et al.* 1994).

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beneath north and south America, their surrounding oceans and parts of Africa and Eurasia from inversion of travel times of horizontally polarized shear body waves. He noted that the upper 400 km is dominated by lateral variations that correspond to surface tectonic environments. He observed that three shields on three separate continents have higher than average velocities down to a depth between 320 and 400 km. Young tectonically active regions are very slow in the upper 250 km. The transition zone between 400 to 660 km depth is a most poorly resolved region. He observed that there is a high velocity layer beneath western South America in the transition zone and is probably associated with a subducting slab. The velocity in the transition zone beneath the western and central part of north America is also faster than average. According to Grand (1994), the lower mantle is dominated by large scale sheets of higher than average velocity and more equidimensional regions of slow velocity. He found that from South America to Siberia, sheet like high velocity anomalies are present from 750 km depth to the core-mantle boundary. Such a low mantle high-velocity anomaly was observed beneath southern Eurasia also. According to him the high-velocity lower mantle anomalies may be associated with subduction during the last 150 Ma.

Anisotropy within inner core was first suggested by Morelli *et al.* (1986) support inner core anisotropy with a symmetry axis, roughly aligned with the rotation axis of the earth. There is nearly 3% anisotropy throughout much of the inner core. P-velocity anomalies as large as 3% are rare in the deep earth and their existence within the inner core is intriguing. Proposed mechanisms for inner core anisotropy are associated with proffered alignment of hexagonal close-packed (E) iron (Jeanloz and Wenk, 1988).

Phase Transformation of Different Silicates and their Relevance in Terms of Seismological Discontinuities within the Mantle : Jeffreys (1937) suggested that rapid increase of seismic velocity at a depth of about 400 km (the 20°C discontinuity) is related to possible conversion of $(Mg, Fe)_2SiO_4$ with orthorhobmic symmetry to spinel-type of structure. Jeffreys' conclusion was based on the observation of Bernal (1936), who predicted that olivine might transform under high pressure to a spinel-like polymorph. Bernal's views were based on the occurrence of two polymorphs of Mg_2GeO_4, one with orthorhombic symmetry (olivine) and the other spinel-type structure. Bernal further suggested that transformation of olivine to spinel-type of structure should be associated with 9% increase in the density.

Akimoto and Fujisawa (1966, 1968) studied the system $Mg_2SiO_4 - Fe_2SiO_4$ up to a pressure of 95 kbars. They also presented phase relations of the system at 800°, 1000° and 1200°C isothermal sections under different pressures as a function of mol%. Ringwood and Major (1972) studied phase relation of the same system as a function of pressure and mol%, and supported the conclusion of Akimoto and Fujisawa. The isothermal (800°C) and polybaric phase diagram of the system as determined by the latter workers are only given (Fig. 2). The figure shows the conversion of olivine (a) with orthorhombic structure to that of modified spinel (b) and

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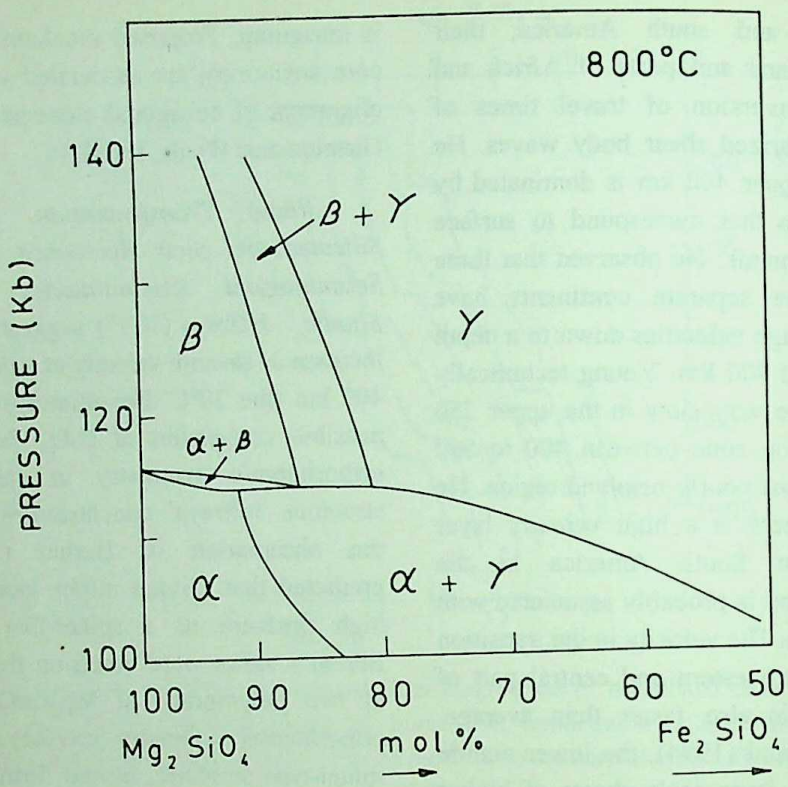

Fig. 2–The system Mg_2SiO_4-Fe_2SiO_4 at variable pressures and 800°C (after Akimoto and Fujisawa, 1966).

finall spinel-like structure with increase of pressure.

After olivine the most inportant mafic minerals is orthopyroxene (a solid solutions of $MgSiO_3$ – $FeSiO_3$). Ringwood and Major studied the binary system $MgSiO_3$ – $FeSiO_3$ at 1000°C under variable pressures up to 200 kb (Fig. 3). Their results show that in this join, near the $FeSiO_3$ end, $MgSiO_3$ breaks down to spinel and stishovite. Following reaction may be noted in this regard :

$$\underset{\text{Pyroxene}}{(Mg, Fe)_2Si_2O_6} \Leftrightarrow \underset{\text{Spinel}}{(Mg, Fe)_2SiO_4} + \underset{\text{Stishovite}}{SiO_2}$$

Clinopyroxene of composition (Mg, Fe)$_2$Si$_2$O$_6$) is present at relatively lower pressure (< 100 kb), but the stable assemblage in the intermediate P-T range is constituted of spinel, clinopyroxene, and stishovite.

Ringwood (1967) noted that a glass of composition $MgSiO_3$ with 10% Al_2O_3, was converted to a single phase garnet instead of an assemblage comprising pyroxene and pyrope garnet.

Conversion of $MgGeO_3$ pyroxene to ilmenite-like structure takes place at of 25 to 30 kb and 700°C (Ringwood and Spearbook, 1962, 1963). On the basis of this observation, they thought that $MgSiO_3$ pyroxene should also be converted to a phase having

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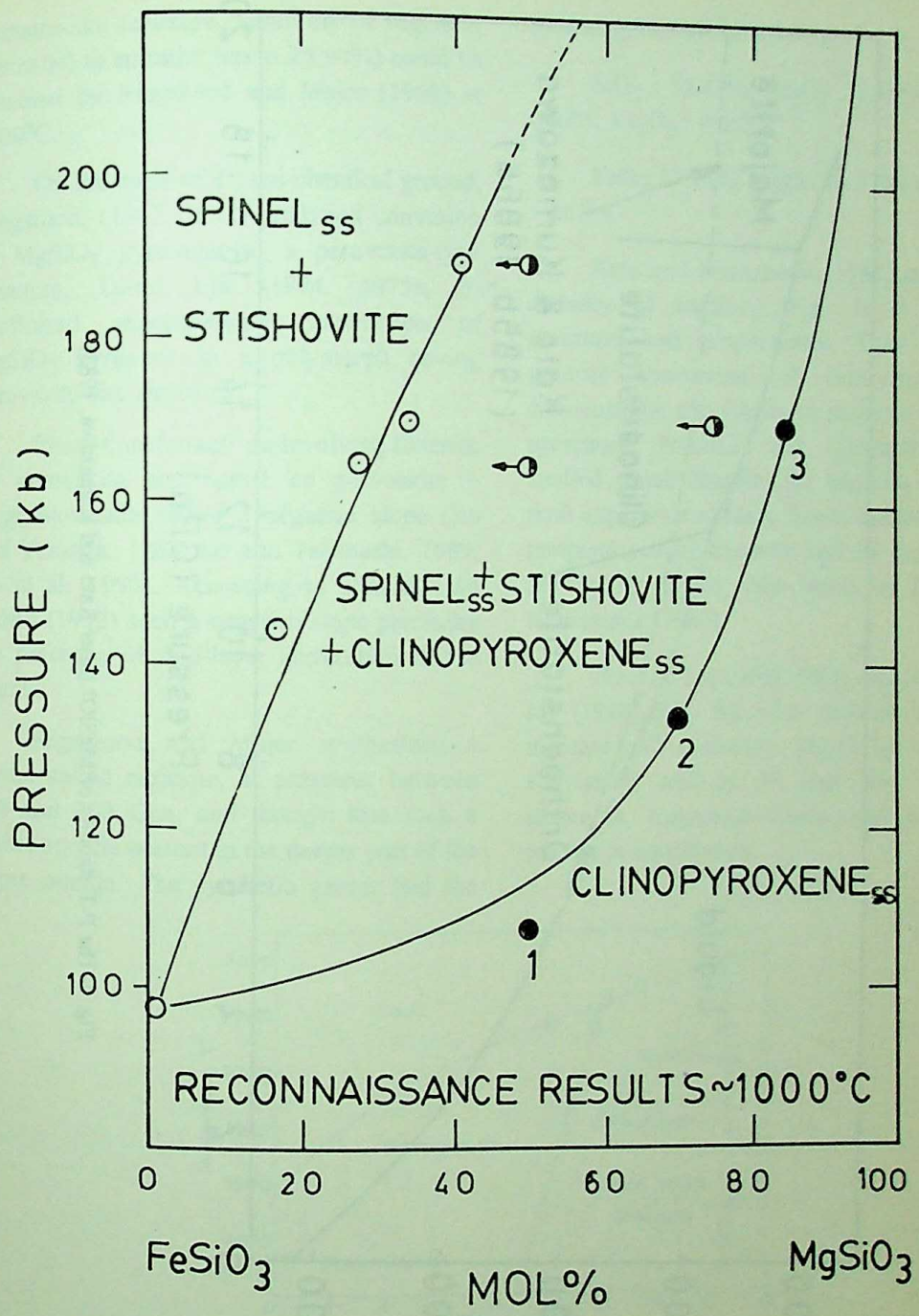

Fig. 3– The system $MgSiO_3$-$FeSiO_3$ as a function of pressure and composition at 1000°C (after Ringwood and Major, 1972).

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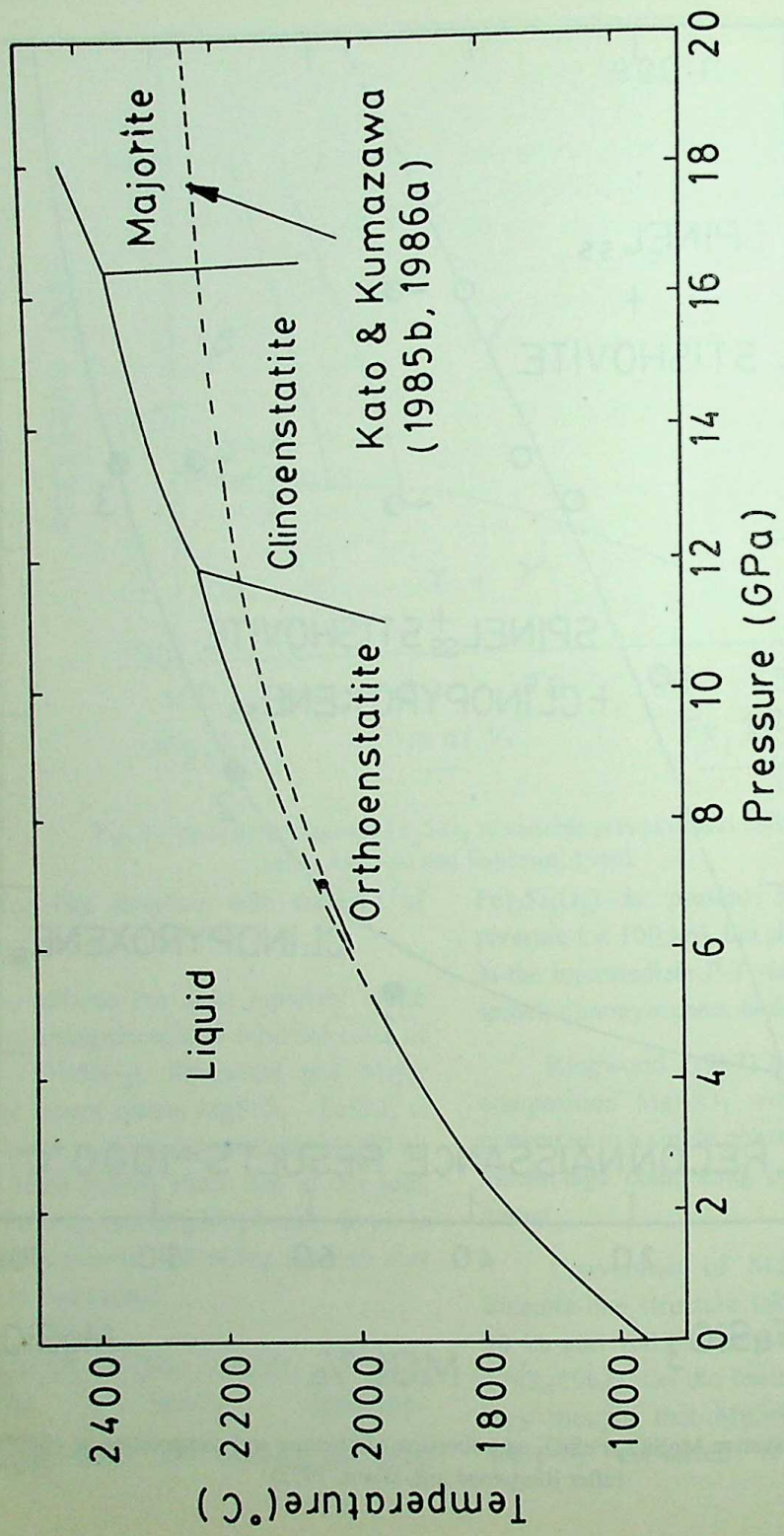

Fig. 4–The P-T stability of $MgSiO_3$ (after Kato and Kumazawa, 1985).

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ilmenite-like structure. Solubility of $MgGeO_3$ (ilmenite) in enstatite (up to 25 wt%) could be obtained by Ringwood and Major (1968) at 1000°C.

On the basis of crystal-chemical ground, Ringwood, (1962, 1974) predicted convesion of $MgSiO_3$ pyroxene to a perovskite-type structure. Later, Liu (1974, 1975a, b) confirmed experimentally conversion of $MgSiO_3$ pyroxene to a polymorph having perovskite like structure.

Phase transformations involving Ilmenite ⇔ perovskite and spinel ⇔ pervoskite + magnesiowustite, have a negative slope (Ito and Yamada, 1982; Ito and Takahashi. 1989; Ito et al. 1990). According to Hemley and Cohen (1992) such a negative slope precludes the presence of two-layer convection in the mantle.

Rignwood and Major synthesized a garnet called majorite, at pressures between 200 and 300 Gpa, and thought that such a garnet may be persent in the deeper part of the upper mantle. The synthetic garnet had the following composition :

SiO_2 : 52.43%, Al_2O_3 : 2.46%, Cr_2O_3 : 0.62%, Fe_2O_3 : 0.65%,

FeO : 17.14%, MgO : 26.07%, and Na_2O : 0.63%.

Kato and Kumazawa (1985) studied the stability of $MgSiO_3$ (Fig. 4) at different pressures and temperatures. They observed gradual conversion of orthoenstatite to clinoenstatite and finally to majorite at higher pressures. Presnall and Gasparik (1990) studied phase diagram for $MgSiO_3$ (Fig. 5); their experimental study shows that the melting temperatures of enstatite and its polymorphs are 160°C higher than those of Kato and Kumazawa (1986).

The join MgO-FeO-SiO_2 was studied by Ito (1984, Fig. 6), who showed that with increase of pressure, Mg_2SiO_4 spinel is eliminated, and at 26 Gpa and 1373 K, stishovite, magnesio-wustite and perovskite coexist in equilibrium.

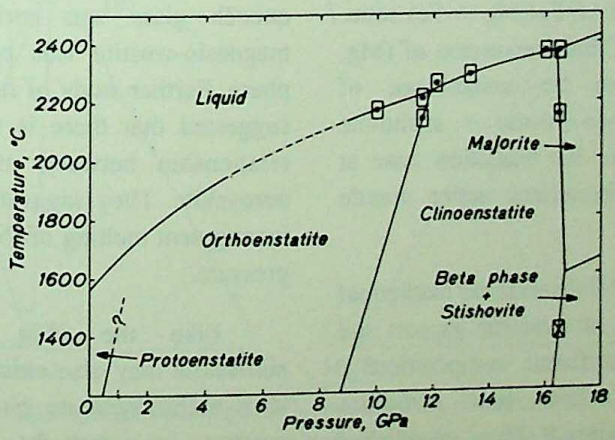

Fig. 5. Phase diagram for $MgSiO_3$ (after Presnall and Gasparik, 1990).

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The join Mg_2SiO_4-Fe_2SiO_4 was investigated later by Ito and Takahashi (1989), who found that above 24.5 Gpa. $(Mg,Fe)_2SiO_4$ breaks down to three different assemblages with increasing Fe/(Mg + Fe) ratio (Fig. 7a and b). Formation of assemblage 1 (perovskite and magnesio- wustite can be explained by the following reaction :

$$\underset{\text{Spinel}}{(Mg,Fe)_2SiO_4} = \underset{\text{Pervoskite}}{(Mg,Fe)SiO_3} + \underset{\text{Magnesio-wustite}}{(Mg,Fe)O}$$

Formation of assemblage 2 (perovskite + magnesio-wustite + stishovite) can be represented by the following reaction :

$$\underset{\text{Spinel}}{2(MgFe)_2SiO_4} = \underset{\text{Pervoskite}}{(Mg,Fe)SiO_3} + \underset{\text{Magnesio-wustite}}{3(Mg,Fe)O} + \underset{\text{Stishovite}}{SiO_2}$$

In this join, $(Mg, Fe)_2SiO_4$ spinel occurs below 24.5 Gpa (1100°C isothermal section), and below 23 Gpa (1600°C isothermal section; Fig. 7), $(Mg,Fe)_2SiO_4$ spinel breaks down to [(Mg, Fe)O, magnesio-wustite)] + pervoskite (1), perovskite + magnesio wustite + stishovite (2) and magnesio wustite + SiO_2 (stishovite) (3) with the increase of Fe/(Mg + Fe) ratio. These results suggest that conversion of $(Mg, Fe)_2SiO_4$ (spinel) to an assemblage of perovskite + magnesio-wustite + stishovite may be reponsible for the transition zone at 670 km, which differentiates upper mantle from the lower one.

Yagi *et al.* (1987) determined isothermal compressional curves of synthetic garnets and majorites for four different compositions : Pyrope, almindine and two majorites ($En_{58}Py_{42}$ and $Fs_{10}Alm_{82}$). They established that these majorites have cubic symmetry. Uchiyama *et al.* (1992) synthesized majorite at 20 Gpa and 2200°C and determined the bulk modulus of majorite (160), which is less than that of pyrope by 6%. A mixture of garnet and mojorite (mixed in variable proportion) may therefore, cause variation in the elastic property of the mantle.

Considerable amount of information is now available regarding melting and phase equilibria relations of silicate perovskite. The data are summarized by in Fig. 8. The melting curve of $(Mg, Fe)SiO_3$ to 60 Gpa was determined by Heinz and Jeanloz (1987). They showed that melting is independent of pressure above 30 Gpa (Tm ~ 3000 K). Later studies by Bassett *et al.* (1988) support the results of Heinz and Jealoz. Above 50 Gpa, there is slight increase in the melting temperature of $(Mg, Fe)SiO_3$ (Knittle and Jeanolz, 1989). Subsequent studies by Ito and Katsura (1992) showed that melting of $MgSiO_3$ occurs at 2870 K, and between 21-25 Gpa, the melting curve has a slope. Williams (1990) studied a composition $(Mg_{0.88}Fe_{0.12})SiO_3$ at 50-55 Gpa using a laser-heated cell, which shows that the quench glass was enriched in SiO_2 and magnesio-wustite was present as a liquidus phase. Further study of Ito and Katsura (1992) suggested that there is eutectic-type melting relationship between magnesio-wustite and perovskite. They suggested that there may be incongruent melting of $(Mg, Fe)SiO_3$ at higher pressure.

Like the $(Mg, Fe)SiO_3$, $CaSiO_3$ perovskite may also exist in the lower mantle as a major separate phase, which could be present in relatively less amounts than ferro-magnesian silicate perovskite and

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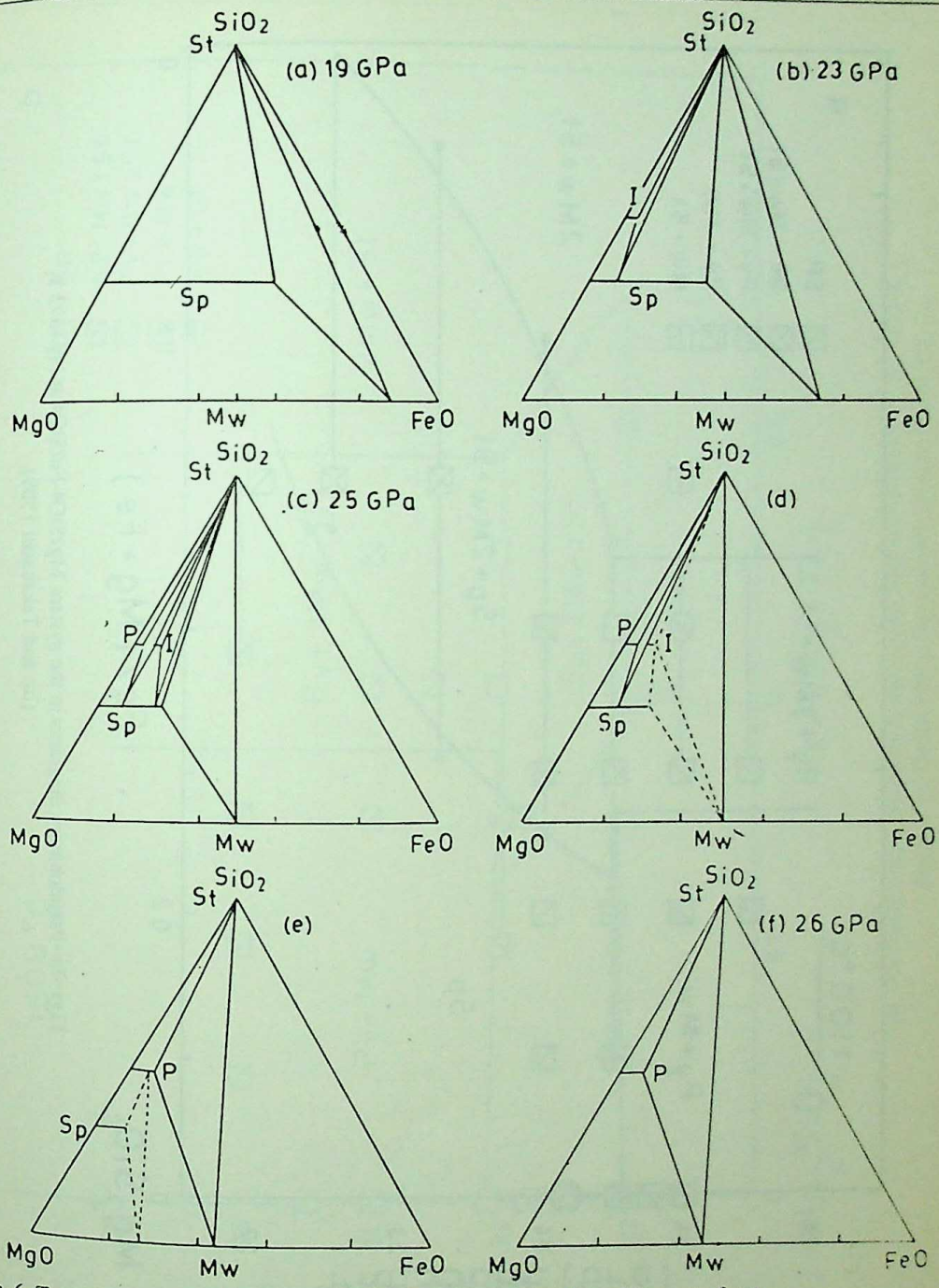

Fig. 6–Ternary system in the system FeO-MgO-SiO_2 as a function of pressure from 19 to 26 Gpa at 1373 K. Sp : Spinel, Mw : Magnesiowustite, St : Stishovite. I : Ilmenite, Pv : perovskite (after Ito 1984).

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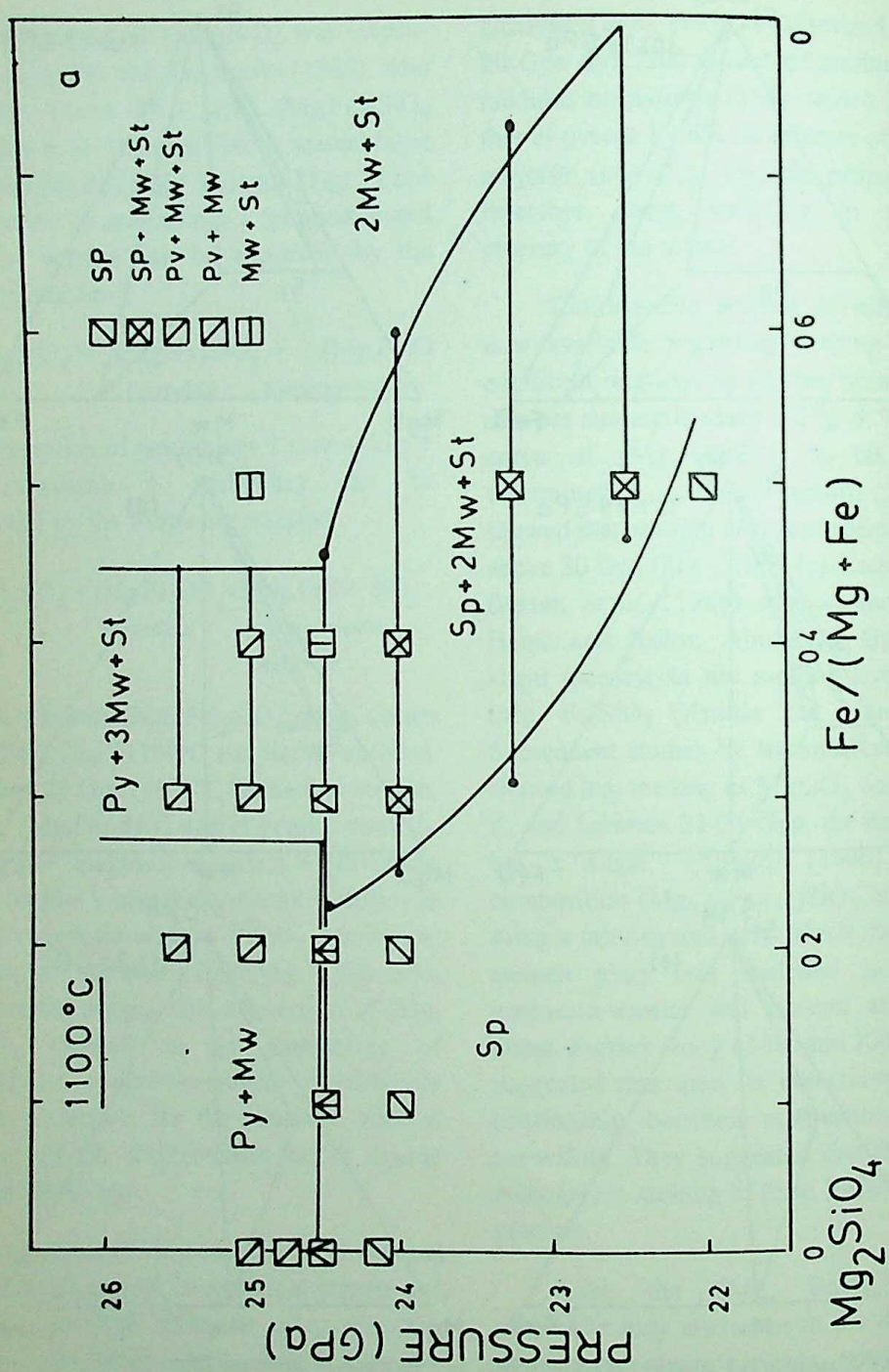

Figs. 7a -Pseudobinary diagrams in the system Mg2SiO4-Fe2SiO4 at (a) 1373 K (Ito and Takahashi 1989).

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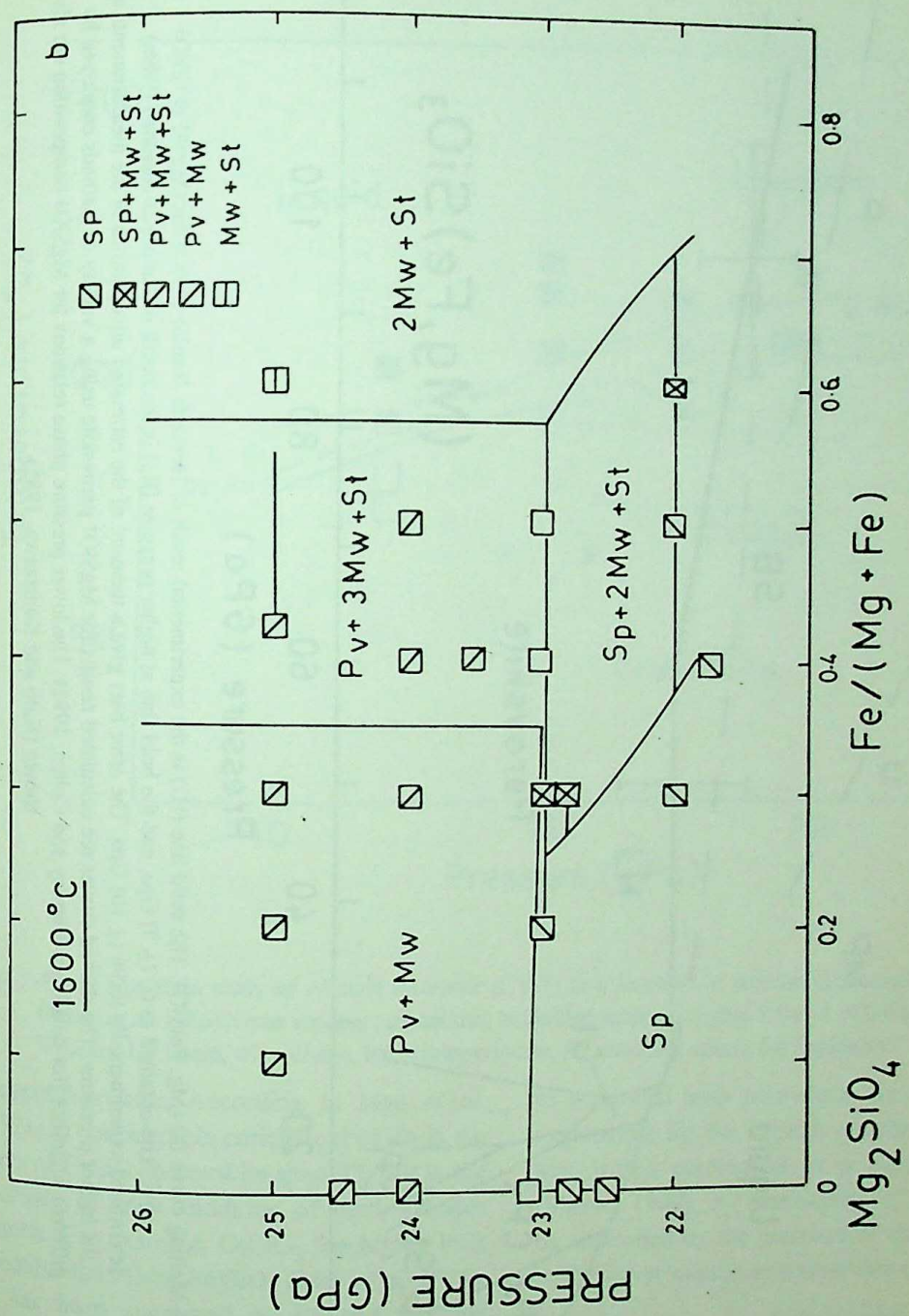

Figs. 7b–Pseudobinary diagrams in the system Mg2SiO4-Fe2SiO4 at (b) 1873 K (Ito and Takahashi 1989). Symbols are same as that at Fig. 7a.

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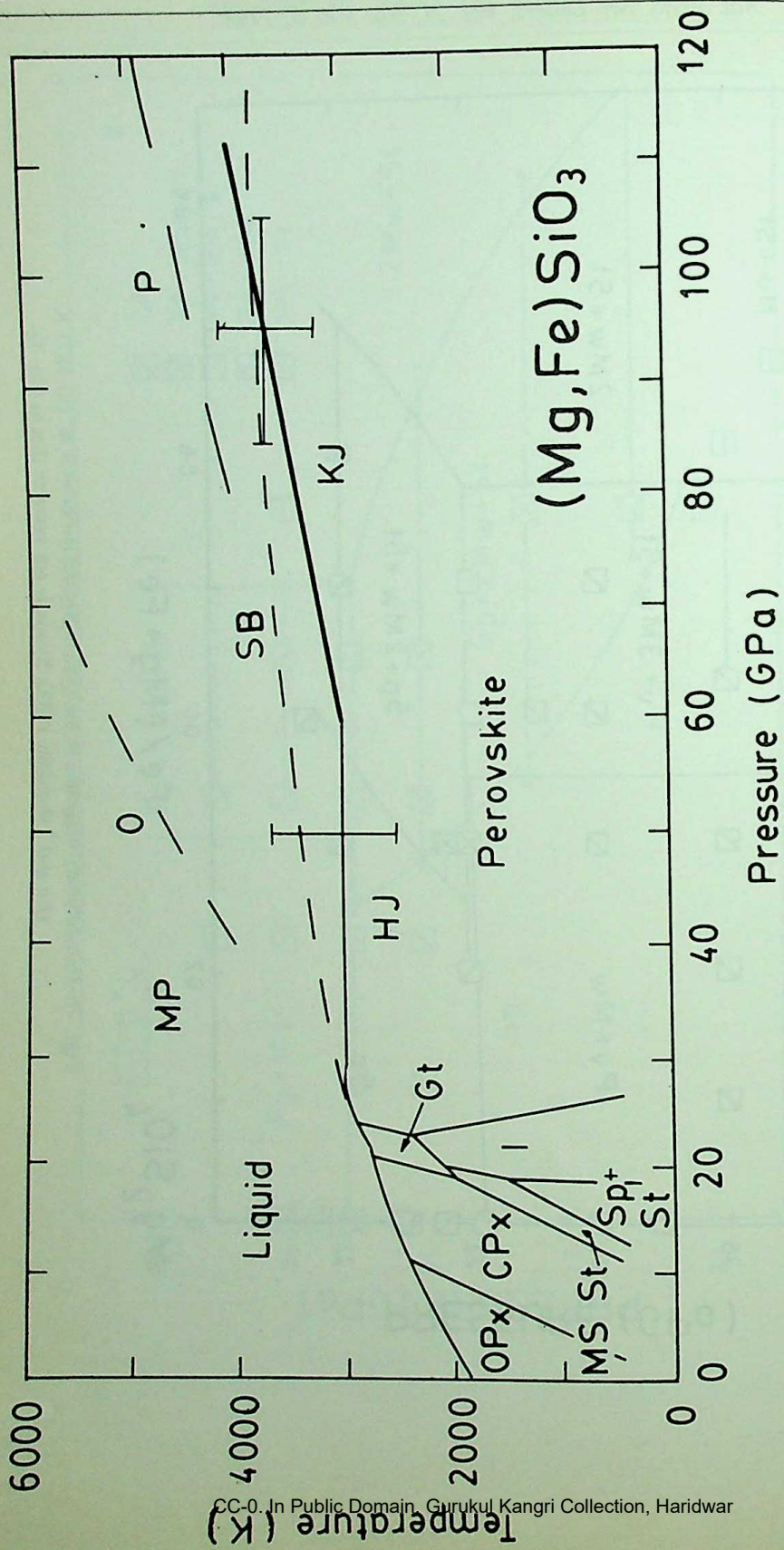

Fig. 8–Melting curve for (Mg, Fe)SiO_3. The solid line (HJ) is the experimental result of Heinz & Jeanloz (1987) for $(Mg_{0.9}Fe_{0.1})SiO_3$ perovskite obtained to 60 (± 5) Gpa, and the bold line at higher pressure (KJ) is the result of Knittle & Jeanloz (1989a) determined experimentally to 96 (± 10) Gpa. The error bars give a measure of the estimated uncertainties in the measurements at the higher pressures. The dashed curves are calculated results for $MgSiO_3$ perovskite using a variety of methods employed by different scientists (for detail, see Hemley and Cohen, 1992). The lower pressure phase relations for $MgSiO_3$ composition are also shown (Kato and Kumazawa, 1985).

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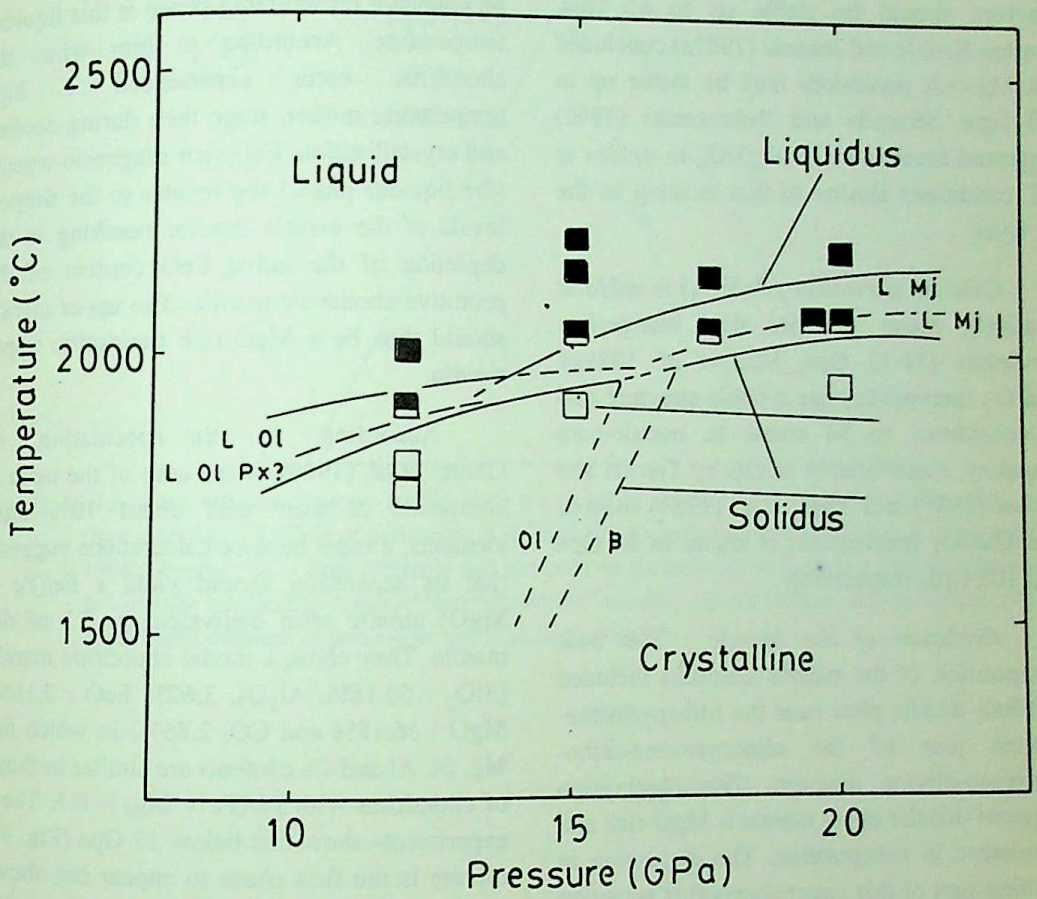

Fig. 9–Phase equilibria study of Allende meteorite (CV-3) as a function of pressure and temperature (after Ohtani *et al.* 1986). Open squares : subsolidus, half-filled squares : crystal + liquid, filled-squares; super liquidus, L : liquid, 01 : olivine, Px : clinopyroxene, B : modified spinel, Mj : majorite.

magnesio-wustite. According to Mao *et al.* (1991), a considerable enrichment of Ca in the form of $CaSiO_3$ perovskite should result in the increase of bulk modulus of earth's lower mantle. For example, $CaSiO_3$ has higher bulk modulus than (Mg, Fe)SiO_3 (Mao *et al.* 1991). It has been suggested by Ita and Stixrude (1991) that conversion of $CaSiO_3$ (pyroxenoid) to a mineral with perovskite-like structure is responsible for the seismic structure near 520 km; which correspond to a transition zone (Sherar, 1990). As partitioning of REE could be controlled by the presence of cubic $CaSiO_3$ in the lower mantle as a reservoir of REE.

On the basis of their studies on (Mg, Fe)SiO_3 (pervoskite), Mao *et al.* (1977)

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suggested that such silicates with pervoskite structure should be stable up to 60 Gpa, whereas Knittle and Jeanolz (1987a) concluded that Mg-rich pervoskite may be stable up to 100 Gpa. Stixrude and Bukowinski (1990) suggested breakdown of $MgSiO_3$ to oxides at P-T conditions similar to that existing in the D" layer.

Calcium pervoskite ($CaSiO_3$) is stable at relatively lower pressure than mangesium pervoskite (11-13 Gpa, Mao *et al.* 1989a). $CaSiO_3$ (pervoskite) has a cubic structure and is considered to be stable to mantle-core boundary. Experimental results by Terrida and Richet (1989) and Yagi *et al.* (1989) showed that $CaSiO_3$ (pervoskite) is stable to 94 Gpa and 100 Gpa, respectively.

Evolution of the Mantle : The bulk composition of the mantle xenoliths included in alkali basalts plots near the orthopyroxene-olivine join of the clinopyroxene-orthopyroxene-olivine diagram. This observation suggests that the upper mantle is MgO-rich and peridotitic in composition. The discussion in the first part of this paper shows that accretion of carbonaceous chondrites is considered to be responsible for the formation of terrestrial planets. Table 1, however, shows that FeO content of carbonatites is 3.5 times that of average peridotite xenoliths, included within alkali basalts. The question therefore, arises as to why the upper mantle is more enriched in MgO over FeO compared to a carbonaceous chondrites,- this needs explanation.

Agee (1990) made high pressure melting experiments on the Allende (CV-3) carbonaceous chondrites at 24, 26 and 26.5 Gpa. He established that FeO-rich magnesio wustite is an abundant crystallizing phase at this liquidus temperature. According to him when the chondritic earth experienced a high temperature molten stage then during cooling and crystallization, FeO-rich magnesio-wustite (the liquidus phase) seg regates to the deepest levels of the earth's interior resulting in the depletion of the initial FeO content of the primitive chondritic mantle. The upper mantle should thus be a MgO-rich peridotitic upper mantle.

According to the speculation of Ohtani *et al.* (1986), if the core of the earth is composed of iron with about 16% light elements, a mass balance calculations suggests that its separation should yield a Fe/(Fe + MgO) atomic ratio equivalent to 0.1 of the mantle. They chose a model chondritic mantle (SiO_2 : 50.18%, Al_2O_3, 3.62% FeO : 7.16%, MgO : 36.18% and CO, 2.86%) in which the Mg, Si, Al and Ca contents are similar to those of chondrites with Fe/(Fe + Mg) = 0.1. Their experiments show that below 13 Gpa (Fig. 9), olivine is the first phase to appear but above this pressure, majorite [(Mg, Fe)SiO_3; with garnet like structure] is the liquidus phase. Their electron microprobe analyses of the liquid (in equilibrium with majorite) show that it is of peridotitic compositions.

During thermal evolution of the earth the outer layer may have been in liquid state up to a depth of about 1000 km or more. The study of Ohtani et al. suggest that at pressure above 13 GPa (equivalent to a depth of 400), Fe-rich majorite crystalizes first. They assumed that Majorite will sink toward the lower part of the mantle and will leave behind a peridotitic

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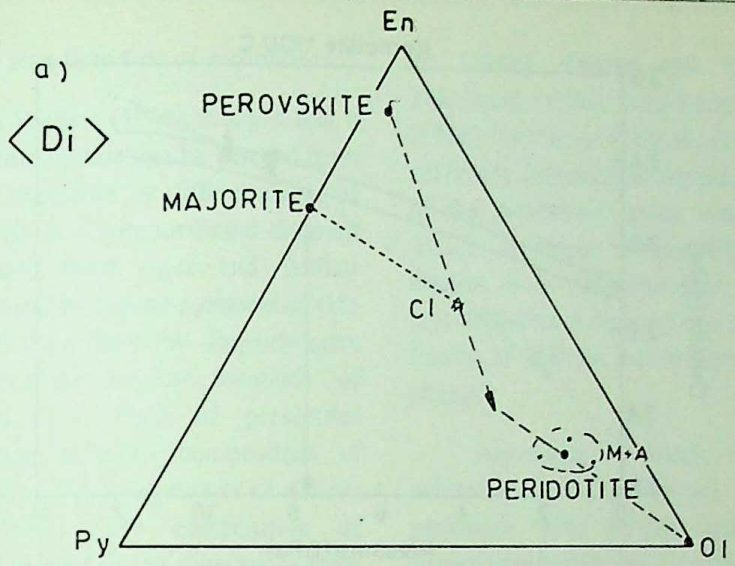
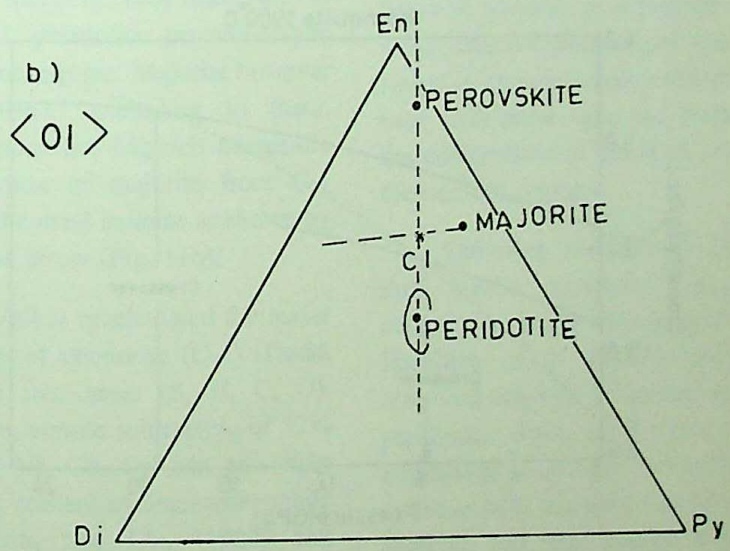


Fig. 10 (a)–Comositional diagram (wt%) from the enstatite-olivine-pyrope-diopside tetrahedron, projected from diopside. The field of peridotites is defined by xenolith averages (for detail see Agee and Walker, 1988). Average Cl is from literature that has been recalculated as described in the text. Cl composition is vartually identical to "cosmic" and "chondritic" mantle. Arrows indicate that peridotite is the result of Cl being depleted in perovskite and enriched in olivine.



(b)-Compositional diagram (wt%) from the estatite-olivine-pyrope- diopside tetrahedron, projected from olivine. Dashed line illustrates coplanarity of Cl, peridotite, perovskite, and the projection point, olivine. Majorite plote off the plane; majorite depletion of Cl upsets the mass balance as shown by the direction of the arrow.

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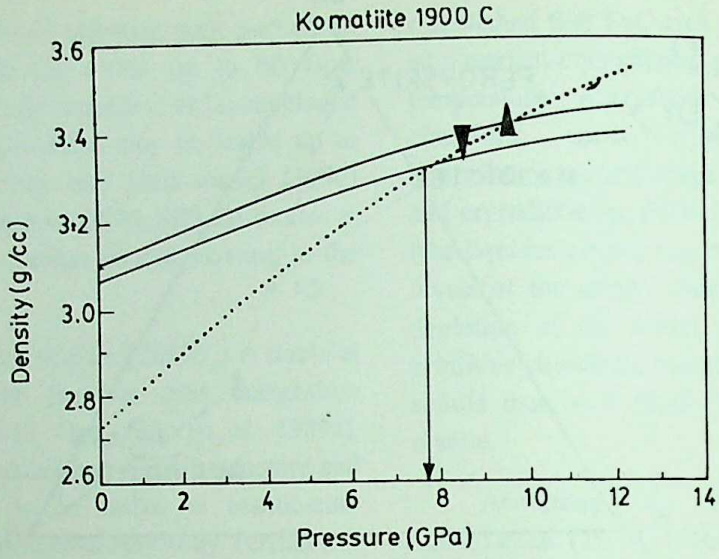
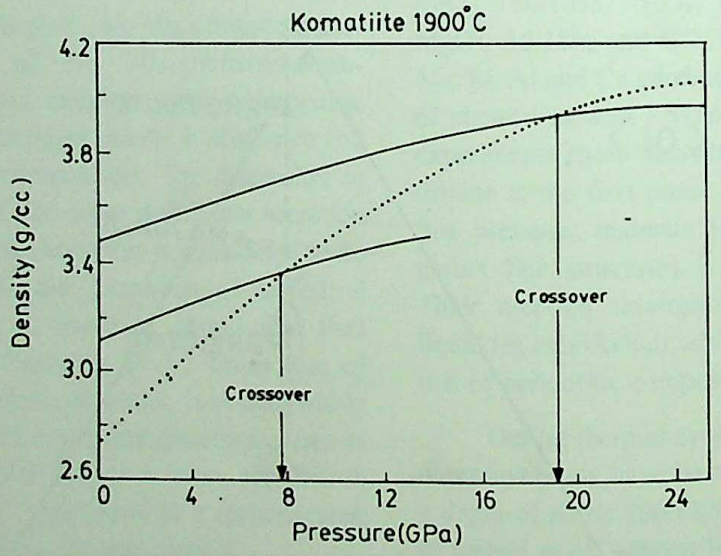


Fig. 11 (a)–Density versus pressure diagrams demonstrating olivine/liquid density crossovers at mantle pressure in komatiite and peridotite, (a) San Carlos olivine (~Fo_{90}) floats in komatiite at 9.3 Gpa, hence equilibrium olivine (Fo_{93}) is neutrally buoyant in komatiite melt near 7.8 Gpa.



(b) At 8.4 Gpa garnet with the composition" 84% pyrope, 8.2% almandine and 7.8% grossular, is the liquidus phase in komatiite, B-4. The density crossover between the experimentally observed garnet and komatiite melt occurs near 19.5 Gpa. If the equilibrium garnet becomes increasingly majoritic with pressure then the density crossover may occur at a pressure lower than 19.5 Gpa.

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liquid poorer in iron than that of a chondrite.

Agee and Walker (1988) thought that a Mg-rich peridotitic mantle can be derived from a carbonaceous chondrite by differentiation of the earth. Fig. 10, is a compositional diagram (wt %), obtained from Agee and Walker (1988). It is a enstatite-olivine-pyrope-diopside tetrahedron projected from the diopside apex (calculated according to the methods of O'Hara (1968). The field of peridotites represent average xenolith composition of Maaloe and Aoki (1977), Jagoutz *et al.* (1979) and Irvine (1981). The composition of chondrite (C-1) plotted in the diagram is from Dodd (1981). The arrow (Fig. 10a) indicates that extraction of $MgSiO_3$ perovskite from C-1 chondrite should result in the formation of a peridotitic mantle.

The dashed line (Fig. 10b) illustrates the coplanarity of C-1, peridotite, perovskite and the projection point, olivine. Majorite however plots off the plane. According to them, formation of Fe-poor but Mg-rich ultramafic mantle by extraction of majorite from C-1 chondrite, upsets the mass balance as shown by the direction of the arrow (Fig. 11b).

Agee and Walker recalculated the major element chemistry of chondrite (C-1) (Dodd, 1981) on-volatile free basis (S, H, C, O). According to them, simple subtracting of 32% Fe together with Ni, Co, Cr, Mn and light elements [(for the content of other siderophile and light elements, see Liu, (1980) and Anderson and Bass (1986)] would not yield a peridotite composition.

It requires further progress of subtraction. Experimental studies of Ohtani et al. (1986), Ohtani and Swannto (1987), Takahashi (1986), and Scarfe and Takahashi (1986) and Ito and Takahashi (1987) provides sufficient information regarding the formation of the peridotitic upper mantle, the kind of which is found as xenoliths within alkali basalts. It is observed that with progressive crystallization 1 first, olivine then majorite and finally at 200 kb, perovskite are the liquidus phases.

According to them, mass balance is achieved with appropriate combination of peridotite with olivine and perovskite, as shown graphically by Fig. 10b. They state that the putative parent C-1 is colinear between perovskite and thus coplanar with those of the projection point olivine. Majorite is found to be off this plane, so that significant addition or subtraction of majority will upset the mass balance. Majorite is a mineral with extensive solid solution possibilities and thus varying range of chemical composition is possible. In their calculation Agee and Walker (1988) took the composition of majorite, crystallizing near the liquidus region.

Harzberg and O'Hara (1985) proposed that mantle peridotites are products of cotectic-like melts containing majorite residue. Harzberg *et al.* (1988) claimed that they observed majorite fractionation trend in some peridotites. Agee and Walker (1988) think that a sequence of cotectic-like melts should not be colinear with majorite but should occupy the eutectic. The near cotectic melting suggested by Harzberg and O'Hara (1985) and Harzberg *et al.* (1988), requires presence of such additional phases as beta or gama olivine in addition to majorite. Agee and Walker think

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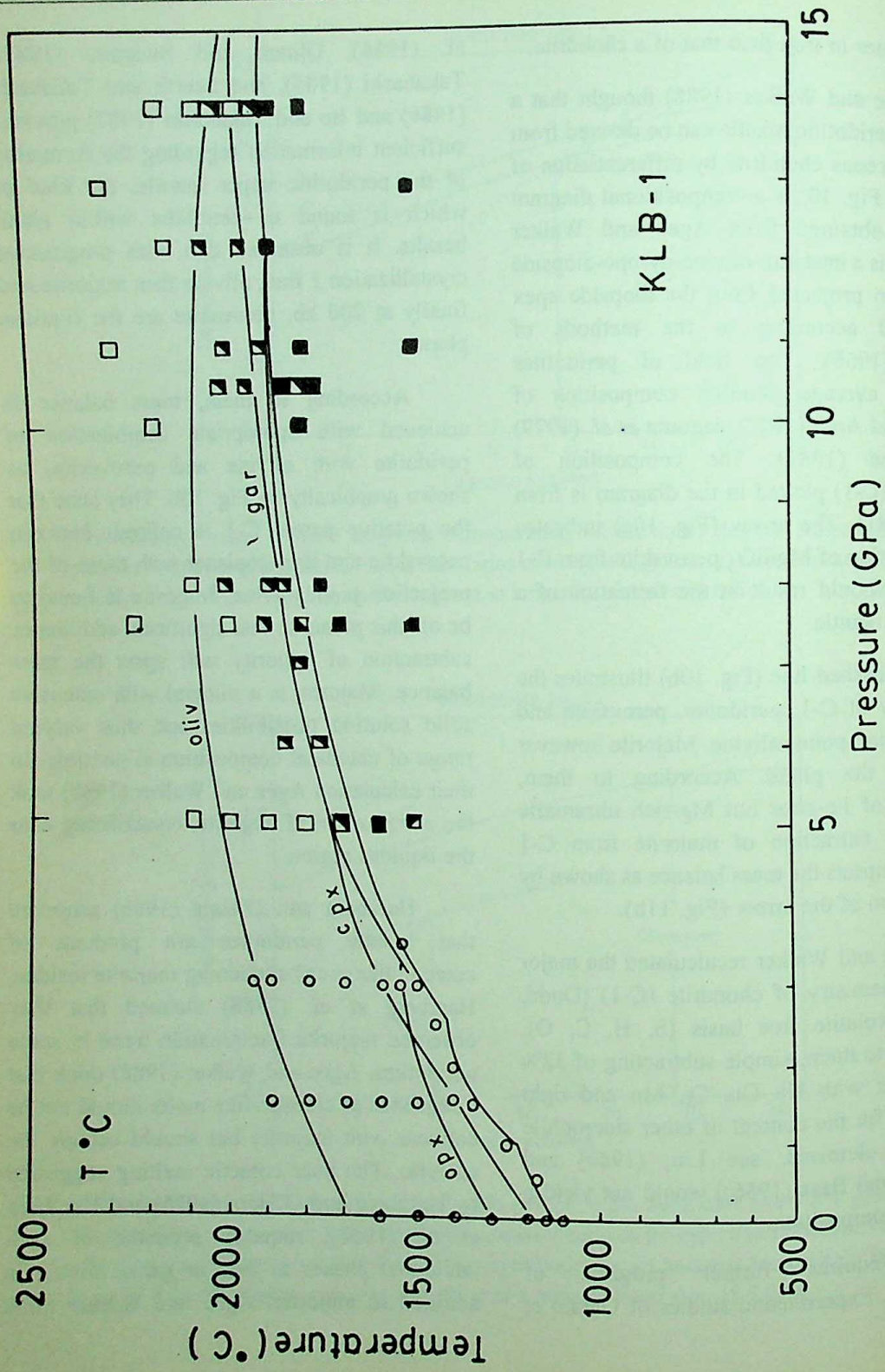

Fig. 12– Phase equilibria study of a meteorite (KLB-1) at variable P-T condition. Oliv : Olivine, Opx : orthopyroxene, Cpx : Clinopyroxene, Gar : Garnet (after Takahashi, 1986).

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that fractionation of only majorite as an independent crystalline phase is not possible, as majorite coprecipitates with other minerals as a polyphase crystalline residue that too near or below the solidus. According to Agee and Walker the liquids can be mechanically separable, but not individual crystals. In case majorite is the only liquidus phase fractionating, then crystallization is not cotectic-like.

Phase equilibria study suggests that from a molten carbonecious chondrite, pervoskite crystallizes at high pressure but is enriched in olivine at low pressure. Stolper *et al.* (1981) proposed olivine flotation hypothesis, which assumes a partially molten earth at depth. The hypothesis suggests that basic silicate liquids should be denser than olivine crystals at pressures between 5-10 Gpa because of their higher compressibility. As the crystals are of lower density, they should rise bouantly (Agee and Walker 1988). Stolper *et al.* envisaged that although at lower pressures crystals have higher density than liquid : with the increase of pressure the density of liquid will rise more relative to crystals and there will be a density cross over, which should have a significant effect on the distribution of chemical components in the crust and the mantle. The pyston-cylinder technique was used by Agee and Walker (1988) to obtain static compression of ultrabasic silicate liquide to 6 Gpa and 2000°C. They measured compression by bracketing, sinking and floatation of olivine crystals to known density run condition. They used komatiite, peridotite and their liquid mixture with Fe_2SiO_4. They used authentic komatitic sample (2-8 b.y. old), which are parts of lava flows from Belingwe, Zimbabwe. They usded a fetile spinel lherzolite sample (KLB-1) from kilbourne Hole, New Mexico. The peridotite and komatiite samples were ground in a mortar and fired at 1076°C under QFM buffer conditions. As a sample of Fe_2SiO_4 synthetic starting materials were used.

In their experiments involving komatiite, peridotitic and liquid mixtures with Fe_2SiO_4, they show constant density changes with pressure at a rate of 0.078/cm^3/Gpa (Fig. 11a, b). It may be observed that in case of a komatitic liquid, density cross-over for olivine and komatiite occur around 8 Gpa, and in case of a peridotite liquid and olivine, the cross-over takes place slightly above 7 Gpa. On the basis of these experiments Agee and Walker (1988) concluded the following :

(a) a buoyant dunite septum was present at the level of 250 km in a primodial magma ocean,

(b) there was buoyant concentration of olivine upward in the early molten mantle followed by stirring of this materials by solid state convection of initially chondritic upper mantle into higher levels, and

(c) trapped densed liquid below dunite might have served as a reservoir for some Archaean komatiite.

Takahashi (1986) studied a peridotite (KLB-1) of composition similar to that expected in the upper mantle. He observed that olivine is the liquidus phase at all pressures (Fig. 12). The second mineral to crystallize with increasing pressure is a Ca-orthopyroxene (up to 3 Gpa), pigeonitic clinopyroxene (up to 7 Gpa) and pyroxene-rich garnet (>

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7Gpa). The melting temperature interval of the peridotite is more than 600°C wide at 1 atm but narrows to about 150°C at 14 Gpa. The partial melts along the peridotite solidus becomes increasingly more MgO-rich as pressure increases. At 5-7 Gpa, the partial melts formed within 50°C of the solidus contain more than 30 wt% MgO, and are similar to Al-depleted peridotitic komatiite, which are common in Archean volcanic terrains. Due to the increase of enstatite component in clinopyroxene solid solution at high pressure and temperature, the orthopyroxene liquidus field narrows, as pressure increases and disappears at 3-5 Gpa. Harzburgites, are common in the peridotites from ophiolite suites. They may represent relicts after separation of the melts formed at depths lower than 100 km. He considers that lherzolites showing protogranular texture, might have been produced as single pyroxene peridotite residues formed by partial melting at relatively greater depths (> 100 km). He also suggests a diapric model consistent with the genesis of a komatiitic magma formed by partial melting of a mantle peridotite at 150-200 depth. Takahashi (1986) made following observations :

(1) convergence of the liquidus and solidus of the peridotites at pressure > 14 Gpa,

(2) the near-solidus partial melt composition very close to the bulk rocks at 14 Gpa, and

(3) change in the liquidus mineral from olivine to majorite garnet at pressures between 16 and 20 Gpa.

Based on above conclusions he proposed that the upper mantle peridotite was generated originally as a magma (or magmas) formed by partial melting of the primitive earth at 400-500 km depth.

In order to clarify the nature of the 670 km discontinuity (Dziewonski and Anderson, 1981) and the state of the lower mantle, Ito and Takahashi (1987) studied the system $MgO-FeO-SiO_2$ and $CaSIO_3-MaSiO_3-Al_2O_3$ at pressures between 10 and 27 Gpa and at temperatures up to 1600°C. According to them the dissociation of the spinel phase into an assemblage of perovskite and magnesio-wustite could be responsible for the 670 km discontinuity. They further established that the dissociation is complete within the pressure interval of less than 1 Gpa; thereby making the discontinuity very sharp. By considering detailed phase relations and estimated physical properties of the minerals crystallizing in the system $MgO-FeO-SiO_2$ at pressures greater than 220 kb. they speculated the mineralogical composition of the lower mantle. In case of the system $CaSiO_3-MgSiO_3-Al_2O_3$, the stability field of majorite was observed to expand rapidly toward the $CaSiO_3-MgSiO_3$ join at pressures between 10-18 Gpa, and retrograde toward the grossular-pyrope join above 23 Gpa, dissociating to an assemblage comprising $MgSiO_3$-rich perovskite and an unquenchable "CaO-rich phase" with diopside like composition. Majorite is therefore, expected to be an important constituent in the transition zone, and the dissociation of majorite could contribute to the 670 km discontinuity. The complete dissociation of majorite however, requires a fairly large pressure interval (~39 Gpa). Its breakdown produces $MgSiO_3$-rich perovskite, a "CaO-rich phase" with small

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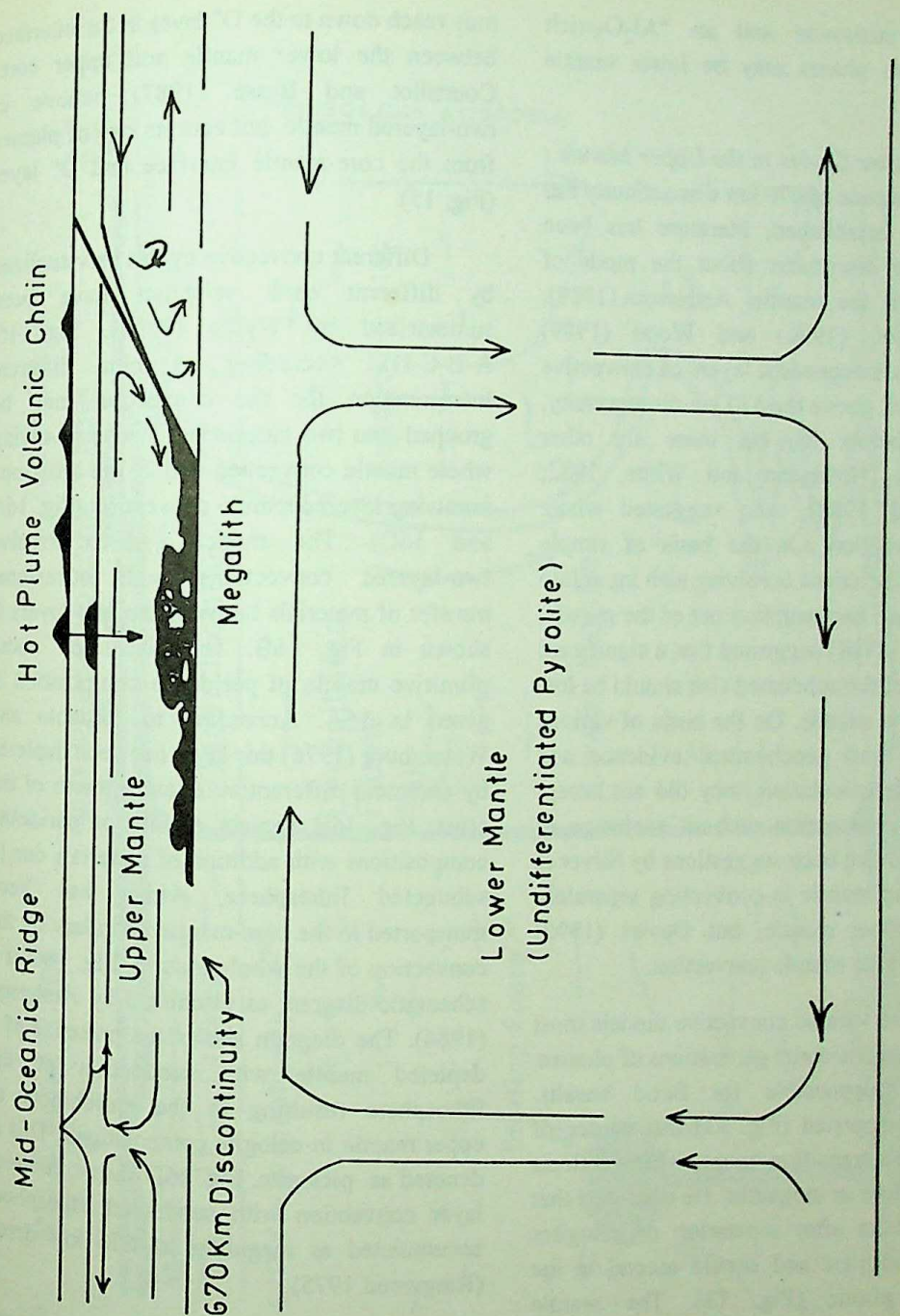

Fig. 13–The "Megalith" model of Ringwood (1982).

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amount of stishovite and an "Al_2O_3-rich phase". These phases may be lower mantle constituents.

Convective Cycles in the Upper Mantle : Once the existence of 670 km discontinuity has been firmly established, literature has been flooded with discussion about the mode of convection in the mantle. Anderson (1989), Knittle *et al.* (1986) and Wood (1989) favoured two independent layers of convective cycles (one set above the 670 km discontinuity, the other below it), but there are other investigators (Hoffmann and White, 1982; Silver *et al.* 1988), who suggested whole mantle convection. On the basis of simple mass flux calculations involving slab input into the mantle and lava eruption out of the mantle, Silver *et al.* (1988) suggested that a significant component of the subducted slab should be lost into the lower mantle. On the basis of various geophysical and geochemical evidence and mass balance calculation, they did not accept two-layered convection without exchange of mass. There have been suggestions by Silver et al. that lower mantle is convecting separately from the upper mantle, but Davies (1990) supported whole mantle convection.

In these various convective models most authors have considered generations of plumes, which are responsible for flood basalts. Ringwood suggested (Fig. 13) that source of plumes is the transition zones, which collects subducted slabs as megaliths. He considers that such megaliths after separation of eclogites would be buoyant and should ascend in the form the plume (Fig. 13). The mantle convection model (Fig. 14) of Devis (1990) on the other hand suggests that subducted material may reach down to the D" layer in the interface between the lower mantle and upper core. Courtillot and Basse (1987) believe in two-layered mantle, but accepts rise of plumes from the core-mantle interface and D" layer (Fig. 15).

Different convective cycles as visualized by different earth scientists have been summarized by Wyllie (1994), Fig. 16, A-B-C-D). According to him different interpretation for the convection may be grouped into two categories, 1) one involving whole mantle convection and 2) the other one involving layered mantle convection (Fig. 16A and 16C). The models, which involve two-layered convections with occasional transfer of materials between the two layers is shown in Fig. 16B. The discussion about primitive mantle of peridotite composition is given in 16A. According to Depaolo and Wasserburg (1976) this layer has been depleted by chemical differentiation and growth of the crust. Fig. 16B depicts mantle of peridotite compositions with addition of materials due to subducted lithosphere, which has been transported to the core-mantle boundary by the convection of the whole mantle. Fig. 16C is a schematic diagram as visualized by Anderson (1984). The diagram shows the presence of a depleted mentle with subduction of the lithosphere resulting in the enrichment of upper mantle in eclogite compositions. This is denoted as piclogite. Fig. 16D shows the two-layer convection with subducted lithosphere accumulated as megaliths at 670 km depth (Ringwood 1975).

According to Fyfe (1994), the earth can lose energy from the interior by two major

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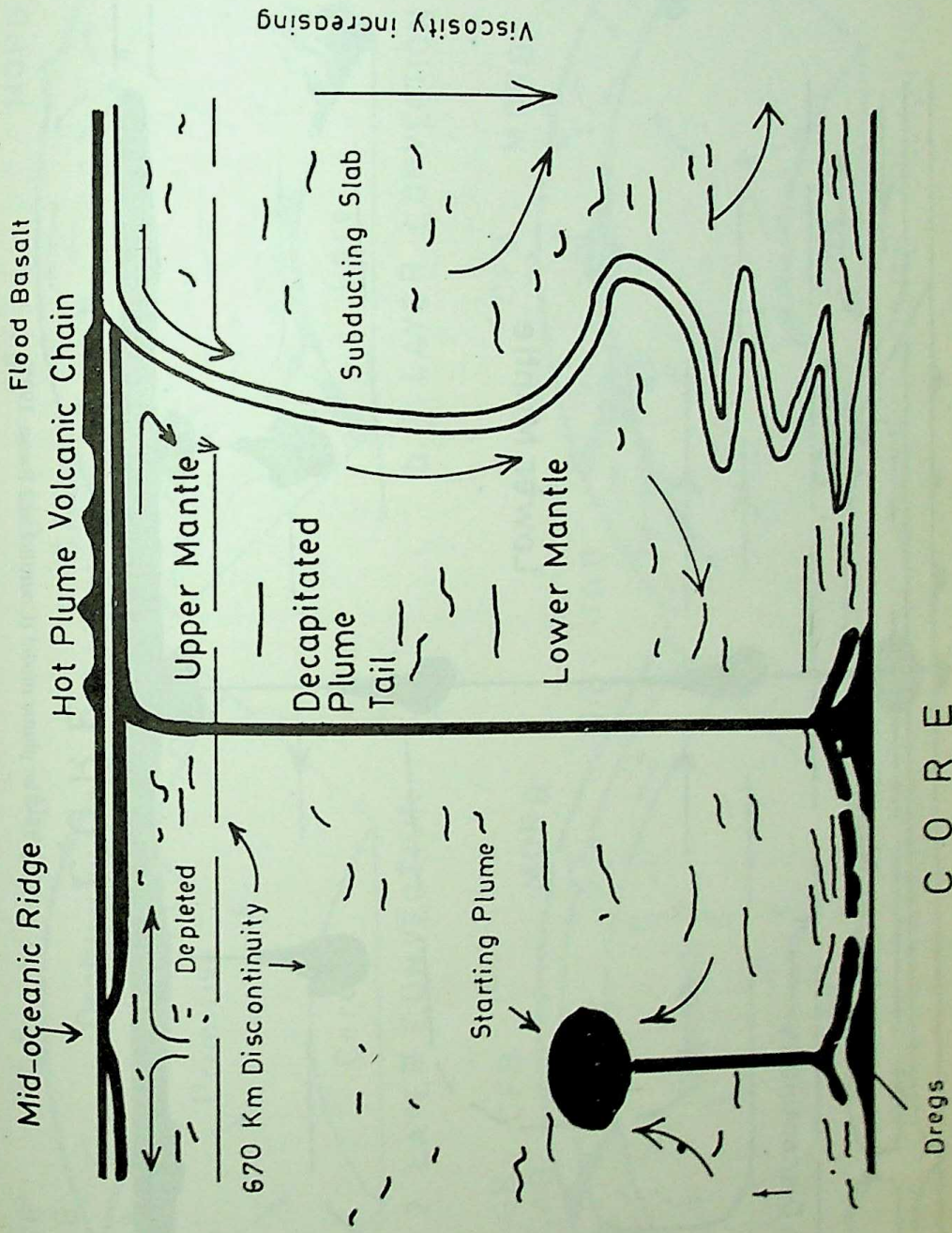

Fig. 14.–The mantle convection and plume model of (after Davies, 1990).

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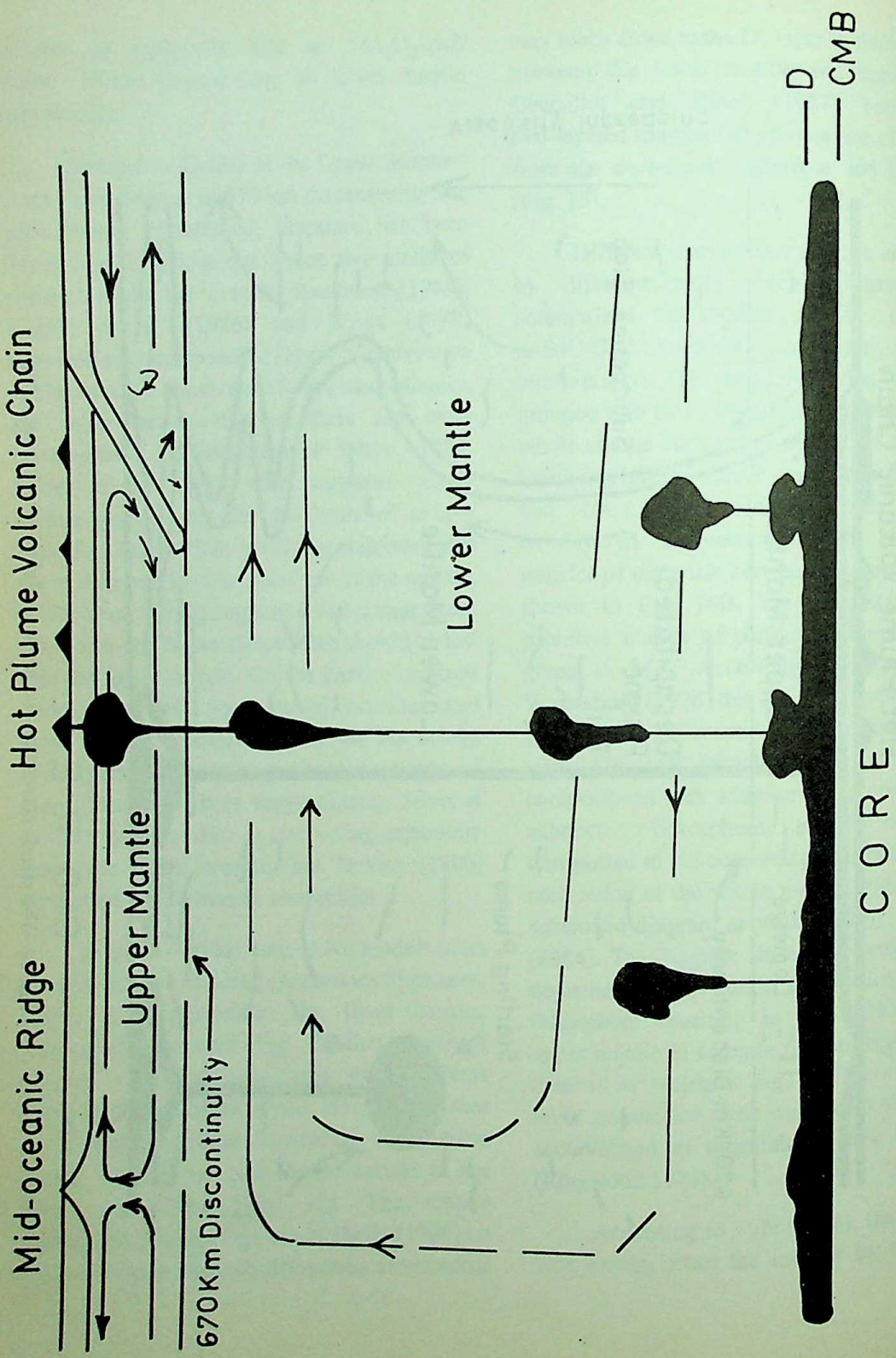

Fig. 15–The plume model (Courtillot and Basse, 1987).

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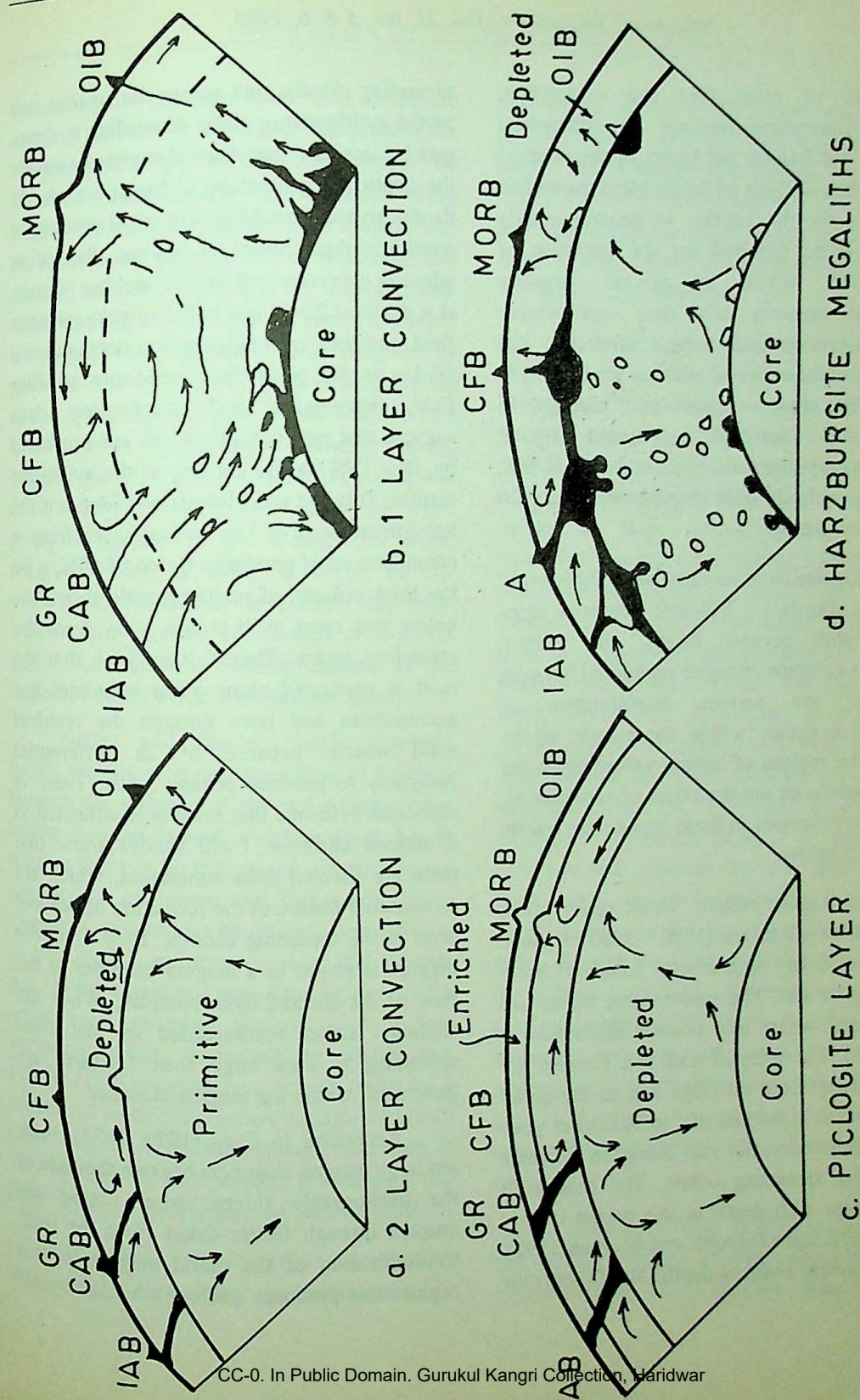

Fig. 16–Convective cycles within the mantle as conceived by different scientists (after Wyllie, 1994).

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processes of conduction and convection. Active convection requires an appropriate Raleigh number for the layers of the interior; and modern analysis of the problem shows that the Ra's for the interior in general greatly exceed those required for the initiation of convection. While in general, pressure increases viscosity, new data high-pressure experimentation and seismic modeling, has shown that the expected increase in viscosity is offset by phase changes and changes in coordination numbers as simple crystal structures dominate materials at depth. In fact, viscosity changes little through the outer 100 km of the mantle.

Magmatism Associated with Differential Tectonic Regimes : Volcanic activities associated with oceanic ridges, rift valleys, different collision zones or regions of hot-spot activities are surface manifestation of convective cycles within the mantle of the earth. The regions of intense volcanism in the plate boundaries are the zones of earthquakes. Volcanic processes in these regions are briefly described below.

(1) *Oceanic ridges :* In all major ocean basins there are ridges (1000 - 3000 m above the ocean floor) with a total length of more than 60,000 km. The mid-oceanic ridges are the regions, where new oceanic lithosphere is generated. The piles of lava thus formed, are pushed away from the ridge axis as the ocean floor spreads at the rate of 1 to 10 cm per year. Hot mantle materials rise along an adiabate below the spreading centre. The change in temperature with depth in this region is only about 0.5°K/km (Turcotte and Morgan 1992). At a relatively shallow depth (50-100 km) the ascending mantle cuts across the solidus and partial melting takes place. According to them, geochemical and petrological studies constrain the depths of generation of basaltic melt. At depths greater than 65-80 km small amount of melting takes place in garnet lherzolite, whereas maximum amount of melting occurs at a depth of 20-65 km in the spinel peridotite field, and little melting occurs at depths above 20 km in the plagioclase peridotite stability field. Petrological and geochemical data suggest that mid-oceanic ridges are produced by 10 - 15% partial melting of the sub-ridge mantle. Turcotte and Morgan consider that for the formation of 6 km oceanic crust from a mean amount of peridotite fusion of 10%, a 60 km thick column of melted mantle should lie below this crust as it moves away from the spreading centre. They further think that the melt is generated along grain bounaries but accumulates and rises through the residual solid matrix because of its differential buoyancy to produce oceanic crust. There is sufficient evidence that magma is collected in a magma chamber. Field stuides show that there are sheeted dyke complexes, which are an essential feature of the formation of oceanic crust at the spreading centres. They think the magma is stored in a magma chamber at the base of the sheeted dyke complex. When the tensional stress accompanied by sea floor spreading is very large then fractures are generated within the magma chamber.

According to Cann (1970, 1974), there are large magma chambers beneath the axes of the mid-oceanic ridges, where lavas are erupted through feeder dykes from the roof. Crystallization of the mafic magma in this region thus produces gabbro, whereas crystal

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fractionation produces mafic and ultramafic rocks at the floor of the dykes. This process has been termed as the "infinite onion model" by Cann as it continuously peels off layers at the edges. Although the generation of magma may be continuous, only batches of liquids ascend upward buoyantly through the asthenosphere after reaching a certain critical size. The supply of magma to any high level reservoir is periodic and the rate of supply is proportional to the spreading rate. Prior to the addition of a new batch of magma to the chamber, the old magma materials already stored in the chamber will undergo fractionation producing more evolved liquids. If the chamber is large, magma mixing is likely to occur. In this process, large axial magma chamber may form. Thus, there may be attenuation of S-waves during earthquakes. Seismic studies in the region of East Pacific Rise support this model.

Nisbet and Fowler (1978) however, thinks that there is no attenuation of S-waves beneath the segment of the mid-Atlantic ridge below *Famous* island, which suggest that at present there is no magma pool larger than 2 km across or below the ridge axis. They therefore, cast serious doubt about the efficacy of this model, and they consider that thermal constraints would not permit the existence of a large axial chamber beneath such a low spreading ridge. According to Nisbet and Fowler (1978) magma rises at high levels by a process of crack propagation through the brittle crust, forming very small storage reservoirs at very high levels; such a model will result in the formation of a poorly layered oceanic crust.

According to Fyfe (1994) convective mass-energy flow from the interior occurs dominantly at the great narrow ocean ridge systems of the Earth (the mid-Atlantic ridge, Indian Ocean Ridge, East Pacific, Rise, etc.), which are dominantly submarine and form the most continuous mountain ranges of the Earth. Some of these extend across nearly almost half the global circumference.

The submarine mountain chains are volcanic with a surface expression of basaltic lava flow. Fifteen km^3 of magma is produced annually along the Earth's ridge because of ascent of hot mantle plumes through pressure release. About 90% of our planet's volcanism occurs at these submarine sites. Ridge volcanism accounts for almost half the heat loss from the planet's interior. Fyfe (1994) thinks that the rising convection cells have roots at depths of several hundred kilometres. Magma batches that rise into the ridges may reach tens of km^3 in volume at any time. Active magma chambers have only recently been mapped and single eruptions of 15 km^3 have been observed. The rocks of the ridge produce a crystalline product of essentially zero age and generate the new crust of the Earth with typical composition. There are small differences in the composition, which rarely departs from the mean for any species by a small percentage. Basalt represents, low melting fraction of the upper mantle beneath oceanic crust. As the basaltic material penertrates to the surface, it pushes the crust apart and causes the process, we now call ocean floor spreading, the driving force of continental drift.

According to Fyfe (1994), early studies of heat flow over and near the ridges produced a great surprise. Given that the rising magmas

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which extrude at and intrude below the surface at temperatures in excess of 1200°C, it would be expected that very high heat flow should be observed.

According to Fyfe (1994) observed that if a hot, porous-cracked and hence permeable, material is placed in a cold liquid (deep ocean water temperatures are normally close to 0°C) cooling will occur by water circulation. The heat flow patterns near the ridges could obviously be explained by the development of large scale convective cooling cells involving the penetration of cold sea water into hot rock. At the Galapagos spreading centre and now in many ridge situations, hot water has been found discharging at temperatures reaching 300-400°C. In some cases, the venting is cataclysmic reaching temperatures in excess of 400°C.

Fyfe (1994) considers that the scale of this water cooling process is impressive, and simple calculation of the energetics reveals that, about half the thermal energy of the hot basaltic liquid is transmitted to the circulating ocean water. On an annual basis, something like 10^{18} g of ocean water can be heated to 100°C, or about one third of the mass to 300°C. The total ocean mass is 1.4×10^{24} g, this means that the entire mass can be processed through the ridges within a few million years, an instant in geologic time scale.

(2) *Magmatism in the rift valley* : The rift valleys are large trough-like valleys formed by subsidence of the floor between subparallel marginal faults. Rift Valleys are zones along which the lithosphere is ruptured because of extension, resulting in the formation of brittle cracks.

Examples of rift systems throughout the world includes, (1) Afro-Arabian rift system (Cenozoic, < (65 m. y.), (2) the Rio Grande rift (Cenozoic), (3) the Rhone depression, (4) the Rhine Graben, (5) the Baikal rift of south eastern Siberia, and (6) the graben systems at Yinchuan, Hetao, Weihe, Shanxi and north China plains (all in the Precambrian north China platform).

Rifts are principally extensional tectonic features. Common association of rifts with extensive volcanism, high heat flow, seismicity and anomalous structure of the crust and the upper mantle provide compelling evidence that rifts are not just phenomena taking place in the upper crust, but are manifestation of dynamic processes in the deeper lithosphere and asthenosphere. Rift systems comprising inter-connected series of rifts are related to lithospheric extension, and may reflect incipient stages of an evolutionary sequence in which continents are rifted apart to create a new interveing ocean. Quite often large volumes of nepheline-normative alkalic basalts, carbonatites and highly potassic mafic and ultramafic lavas are associated with rift valley systems.

(3) *Magmatism associated with collision between two plates :* A very active example of such a situation is that of the Himalays. In case of continent-continent collision, a continental crust may be subducted inspite of its larger buoyancy thickness and rigidity. In such a process a small part of a continental plate may sink at a steep angle or may remain attached to the underside of the other plate. Magmatism in the Himalayan mountain chain resulted in the

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emplacement of S-type granites, which have very high $^{87}Sr/^{86}Sr$ ratios (0.780). The may suggest that the acid magma might have been formed by crustal fusion, during the subduction of the Indian lithosphere below the Siberian plate. Eruption of younger K-rich andesites, dacites and rhyolites took place in the Tibetan plateau as a result of continent-continent collision. In the Himalayan example, a vast metamorphic dewatering and melting event follows the major thrust event.

Collision Between an Ocianic Plate and a Continental Plate : Seismic studies of the oceanic lithosphere and earthquake generation in trench regimes shows that the oceanic lithosphere, about 100 km thick bends and sinks or is thrust into the mantle and the process is essentially initiated along ocean-trench axes.

At subduction zones, the volatile-laden oceanic crust has layers of sediments. Subduction of such an oceanic lithosphere recharges the mantle with volatiles and species like Na, K, U, and carbon and sulphur compounds. Release of the volatiles must induce convection in the overlying mantle and mobilize the most soluble and fusible components eventually leading to the production of basaltic-andesites. Granite-rhyolite production and prograde metamorphism essentially dehydrates the basal crust and leads to host of ore-forming processes.

Similar processes occur during continental collisions (and on a small scale with strike-slip boundaries), where the crust may be thickened to 60-80 km.

The Benioff zone, which underlies the trench defines narrow bands, which are broken apart into different segments 100 to 500 km long and are offset from one another. The arc volcanoes occur located at 30 to 70 km interval. The basaltic rocks near the oceanic trench are quartz-normative and those away from the trench are nepheline-normative. Basalts from these regions are silica-oversaturated compared to basalts of oceanic ridges and back-arc oceanic spreading centres. Island arc lavas are higher in Al, Rb, Sr, Ba, Pb, CO_2 and H_2O and lower in Mg, Ti, P, Zr, Nb, Ni, Cr and have lower K/Rb, Rb/Sr, Fe/Mg, CO_2/H_2O, Cl/F and Sr isotopic ratio.

In the Pacific margin of north and south American continents Precambrian and Palaeozoic rocks have been uplifted, and subjected to volanic activites during late Triassic and early Jurassic. Four magmatic rock types (low K, calc-alkalic, high K and shoshonitic lavas), are typical of island arc environment, and observed in the South American continental margin. In contrast to island arc volcanism, proportion of such silica-rich members as dacite and rhyolites are more abundant in case of the regions associated with continental margin volcanism. Here acid volcanic rocks occur as pyroclastic flow materials in association with zones of thickened continental crust.

There are three linear segments in the Ands; (a) the northern and central volcanic islands, which are 140 km above Benioff zone, which dips 25° to the east; (b) the continental crust in the northern segment, which is 40 to 50 km thick and that in the central part is 70 km thick and (c) the southern volcanic zone,

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which lies 90 km above the Benioff zone. The three portions are separated by two zones which are not associated with volcanism and are undertaken by subduction slabs, that dip to the east. Basaltic andesites and andesites (SiO_2 : 53-61 wt%; $^{87}Sr/^{86}Sr$: 0.7038 to 0.7044) are found in the northern volcanic segments. Earlier, the central part erupted rhyolites and ash flow tuffs but later, the region has been dominated by andesite and dacite volcanism.

(4) *Intraplate Volcanism* : Burke and Wilson (1976) suggested that there are hot spots or mantle plumes, over which the oceanic plate moves. Magmas rising from the plume are responsible for surface volcanism, and a submarine volcano develops, which may eventually result in the formation of an emergent cone. As the volcano is carried progressively away from the centre of the hot spot due to the movement of the lithospheric plate magma supply is cut off and the volcano becomes extinct. This ultimately results in the formation of a chain of extinct volcanoes moving away from the hot spot in the direction of the sea floor spreading (Hawaiian Islands chain). It is observed that Pacific island chains (Hawaiian-Emperor, Gambier-Tuamotu, Austral-Cook and Gilbert-Mershall) change direction from SE-NW to slightly west of north. Such variation in the direction of the chain is related to a change in the direction of spreading of the Pacific plate 40-50 Ma ago. Burke and Wilson recognized a global pattern of 122 hot spots, which have been active during last 10 Ma within both oceanic and continental plates. They identified 53 oceanic hot spots, which have a tendency to be located close to the mid-oceanic ridges.

Kimberlites, carbonatites, feldspathoidal rocks, and A-type granite typically occur in intraplate continental setting, although many of them may occur in other tectonic regions. The vent areas of flood basalts may have been however within continental rifts, that evolved into oceanic margins and may be covered by continental shelf sediments. Thus, the division of some magmatism to cratonic and rift magmatism may be difficult. They seem to have been derived from subcontinental magma source (albeit flood basalts). The source of such magmas have been deep down in the mantle.

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The record of energy and chemical transport and the foundation of mineral resources

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Abstract : Direct observation of processes on modern Earth have shown that the cooling processes lead to geochemical mixing influencing all the geospheres and the continental crust. The chemistry and mineralogy of Earth materials carry the record of the major energy and chemical transport systems. The new techniques of surface analysis often show the nature of fluid-gas phases. In the past two decades the importance of water cooling and hydrosphere interactions with the outer 10 km or so of the crust have explained as host of chemical and isotopic features. Today, new attention is being focused on the role of the biomass in Earth chemistry and the scale of the processes. Almost all of our most basic resources, metals, fossil fuels, fertile soils, involved the interactions of atmosphere, hydrosphere, biosphere, with the outer shells of Earth. New needs in waste management technologies involve use of the same knowledge. While there can be no doubt that the ancient Earth was more energetic, there is still no general agreement on the main styles of convection, perhaps reflecting more chaotic tectonmics. In the next decades there will be vast need for mineral resources and new technologies must be developed to protect the precious land and water resources.

(Keywords : geosphere interactions/convection in planet earth)

Introduction : All phenomenon which change the distribution of the elements on this planet are driven by the fundamental cooling processes and the energy loss pattern of the planet. In his elegant account of the energetics of the Earth, Verhoogen (1980) states "every geological process involves exchange of or transfer of energy in one form or another. Most geological processes thus entail a loss of energy from the Earth". And as stated by Elder (1976), "our earth is a vast machine, insatiably reconsuming itself". Thus, in a general way understanding patterns of energy loss and the geosphere interactions resulting from energy transfer forms the basis of understanding all our basic resources, fertile soil, oil and gas, or gold and geohazards. All involve the motion of geofluids. Work over the past decades has clearly shown that we live on a planet which loses heat from its solid regions by conduction, convection and, in the near surface regions, by interaction with the hydrosphere, often to depths of many kms. It was the classic work on heat flow patterns in the modern ocean floors (Lister, 1977), Boulegne and Pflumio, 1992) that showed the scale of fluid penetration and cooling processes. We now recognize that such

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processes are active over almost the entire surface of the Earth above and below sea level. Also, over the past decades we have recognized that geosphere interactions and recycling, influence the chemistry of the entire planet from core to atmosphere.

Present Geosphere Interactions : Geosphere interactions on a convecting planet of complex chemistry and related physical properties must involve mixing and separation processes. On the planet today the greatest mass- energy transport process occurs at the great ocean ridge systems. Water cooling of the porous-cracked near ridge magmas is estimated to involve something like 150 km^3 of sea water per year. This implies that the entire ocean mass is processed through the ridges in a few million years. Massive chemical exchange processes occur. The basalts absorb H_2O, O_2, CO_2, S, Cl, K, U, Na ... while the dischange fluids are enriched in Ca, Mg, SiO_2, Mn, Fe and a host of trace metals like Zn, Cu, Ag, Au ... (Fyfe and Lonsdale, 1981; Fyfe, 1992, 1994). The processes influence the isotope systematic of many important species ($Sr^{87/86}$). Recent studies show that micro- organisms are involved in a host of processes at temperatures to at least 100°C and below (see biosphere below). A particularly illustrative case is that of SiO_2 in solution. Given the warm-hot water flux at the present time (150 km^3 a^{-1}) at a concentration of 100 ppm (some Galapagos waters contain about 1300 ppm), the silica flux could be of the order of 1.5×10^{13} ga^{-1}, or almost a km^3 of quartz every 100 years or so (if one considers a mountain block, $1000 \times 100 \times 10$ km^3 in volume) of quartz, it could be formed in 10^8 years. It is no problem to form continental (sedimentary) crust on a more energetic earth. Iceland provides a nice example of such processes, (Fyfe 1993). Iceland is particularly interesting in that the recharge zones can be leached and rich in minerals like kaolin while the discharge zones are dominated by silica. Thus, during water cooling, silica-clays are formed, rather good continental crust components. There is no doubt that geothermal cooling fluxes at ocean ridges play a profound role in the chemistry of hydrosphere, biosphere, atmosphere and sediments (Fyfe, 1992). Such processes are often associated with interesting metal separation processes.

As the new ocean crust moves off the ridges heat flow pattern show that fluid interactions continue. But at long distances from the ridges heat flow is often greater than expected (Anderson, 1981). As previously suggested (Fyfe and Lonsdale, 1981) hydration (serpentization) of cool peridotites in the deeper ocean crust is highly exothermic, a process which generates significant heating. And the reaction of sea water with ultramafic rocks can absorb water and produce high salinity fluids as reported by Vibetti *et al.* (1989) in serpentinites of Cyprus. Obviously such types of metal transport are of great importance to ore deposition, particularly when there is an impermeable sediment blanket to throttle rapid discharge as at the near ridge black smokers. The situation off the Juan de Fuca ridge system provides a perfect example. It could well be possible in such systems to simulatneously extract metals and energy. But of great significance is that the cool ocean floor rocks 100's of km off the ridges have a very different chemistry from their parent materials which come from the mantle, changes which involve some very significant

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components such as CO_2, H_2O, S, Cl, K, U ...

Subduction-Mantle Return : It is interesting to reflect on the debate of the past 30 years on the nature of the subduction process. One thing is certain, there is very little old ocean floor mantle derived crust of modern type (ophiolites) on this planet. Most has returned to the mantle. My own interest in this problem developed while I was in California working a little on the Franciscan systems. Gilluly (1971) had written a most interesting paper stating that there were not enough modern sediments on the planet and that a significant quantity must be recycled with the ophiolitic components. We had been impressed by the lack of meta-pelagic sediments, some of which would become kyanite schists, in the metamorphic assemblages. Then came the arguments about the meaning of systems like those of strontium isotopes in andesites which to some, showed that sedi- ments could not be subducted or we would see the results in the andesitic belts. But there is nothing like direct observation ! Thus Hilde and Uyeda (1983) showed that as subduction occurs the bending lithosphere cracks and forms horst and graben structures which can promote the entrapment of massive quantities of sediments in the grabens. The now well documented studies of the Japan trench and its western walls clearly show that there is virtually no sediment accretion but all are underthrust with the ophiolitic rocks. We now know from studies of species like He^3, Be^{10}, that massive subduction of sediments is certain.

The scale of the process is impressive. Thus de Paulo (1988) suggests sediment subduction rates in the range 1-3 km^3 per year. Given that the present continental crust has a mass of about 1.6×10^{25} g, if sediments are subducted at a rate of 6×10^{15} g a^{-1}, the entire present crust could be subducted as sediment in 3 billion years. But given a more vigorous, energetic past convective system, recycling rates could have been an order of magnetic faster. So the question "where has all the old crust gone ?" (Carlson, 1996) is perhaps no surprise. It is interesting to note (Fyfe *et al.* 1984) that the studies in the Japan trench region has suggested to some, that nuclear waste disposal in subduction grabens might be a feasible technology. Recent work of Suyehiro *et al.* (1996) in the Izu-Ogasawam (Bonin) trench system shows massive development of serpentine diapiric systems. As serpentine dehydrates at depth, fluidized bed injection of the light materials is a natural process. Often such systems carry with them high pressure mineral assemblages (Barriga *et al.* 1992). Given such processes, it seems we can probably forget about nuclear waste disposal in trench systems.

The present subduction process raises many questions about the chemical evolution of our planet. At the present time, the growth continents, light, high U, K, SiO_2 materials, is not a one way process. But a particularly interesting case is provided by water. A classic view of hydrosphere evolution was developed by Rubey (1951), who proposed continuous degassing of the earth. But at the present time the earth is also ingassing. Given wet ophiolite, sediment subduction, water is returned to the deeper earth. At the present time the H_2O subduction rate is in the order of 1 km^3 a^{-1}, a rate which would recycle the ocean mass (1.4×10^{24} gm) in a billion years. If the earth is cooling as it mixes, will the ocean mass

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change with time ? It cannot be steady state. A cooler upper mantle could easily absorb all the water in amphiboles, talcs, micas like phlogopite, and hydro-silicates like hydro-garnets (Fyfe, 1992). But some have suggested that we constantly receive a significant water flux from comets and the like. In fact, Frank (1990) suggests that we receive about 1 km^3 per year by these events at the present time ! It is interesting to note the suggestion by Pattou *et al.* (1996) that the present abundance of certain elements like the platinum group in the mantle, may require later addition of such elements. We must visit other planets.

The present subduction regimes show that the ocean lithosphere requires a long travel time to cool and become heavy before subduction is initiated. What would happen if the ridge spacing was much smaller, smaller convection cells. The present discussions involve ridge push and subduction drag in very large cells. It is interesting to note the recent advances in concepts of viscosity and processes in the whole mantle and views that subduction, in part, may go to the core boundary (Kerr, 1996a), while Widiyantoro and Hilst (1966) report seismic evidence for slab penetration to depths of at least 1500 km.

There is no need here for long discussion of the fluid regimes (magma, water) related to subduction zones and their profound importance to the global resource base. Keppler (1996) has described the remarkable chemistry of saline fluids in equilibrium with andesitic magmas (80,000 ppm K, 1321 ppm U, 3204 ppm Pb, 587 ppm Zn ...). There is no problem in taking salt to depth (Plank, 1996). Further, recent studies in the Andes (Beck *et al.* 1996) show the huge thickness of crust with a maximum thickness of 70-74 km, similar to the Himalayas. There must be massive crustal growth by underplating mechanisms. The return flow processes create our regions of high topography and their erosion controls everything forms soil fertility to oil basin formation (Breuer and Spohn, 1995).

Some subduction regimes are associated with massive continental collision events (the Himalayas) or massive strike slip motions (California, New Zealand). In the consideration of the evolution of continental crust the present Himalayan situation is of particular interest. The Himalayan collision has created a region of thick re-worked crust over a section 3000 × 1500 km (equivalent to an area 60% of continental Australia). The metamorphic relaxation processes must be impressive (Allegre *et al.* 1984, Fyfe, 1994). If thermal equilibrium is established in this overthickned crust, the metamorphic dehydration processes can produce about 2×10^6 km^3 of fluid equivalent to 0.1% of the ocean volume or half the mass of the present ice caps. Metamorphism on this scale could change sea level (Fyfe, 1986a). The resource potential of this region is now under intense exploration, particularly in the region of Tibet. On a smaller scale, the thickening processes associated with strike slip faults can cause significant metamorphic fluid flows (Allis, 1981).

The new developments in deep seismic tomography (Dziewanski and Woodhouse, 1987) show that parts of the descending slabs may subduct all the way to the core-mantle boundary. Kendall and Silver (1996) show that

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there may be "slab graveyard" at the core boundary and suggest that some of the seismic properties may indicate the presence of a melt fraction. Thus some mantle plume may root at the core-mantle boundary. The chemistry of the core is not well constrained except that there is general agreement that light elements like C, O, Si, H must be present. It is not difficult to see how hydrogen could be included during core formation (Fyfe, 1987, 1994). If hydrogen is present, and if the core is cooling and the outer shell crystallizing, hydrogen could be evolved, from water, and trigger melting near the core mantle boundary.

The subduction, collision regimes, nicely show how subducted materials, lower crust components, influence the products of partial melting, the high Sr^{87}/Sr^{86} Himalayan granites provide an excellent example. I was intrigued by a recent paper by Edgar *et al.* (1996) on a correlation between fluorine and potassium in alkaline rocks. Halogens are enriched in many marine materials, and if subducted, could greatly influence the mantle halogen budget. Imagine the result of subducting sediments with a large marrine phosphate component (Fyfe, 1983). I am always intrigued by regions with special chemical anomalies that appear to be recycled over long periods of time. The tin belts of China and South-east Asia provide excellent examples (Schwarta *et al.* 1995).

Hot Spots : Hot Spots as with the Hawaiian islands, in a sense represent the random thermal processes in the larger plate tectonic convective processes. As shown by Turcotte and Oxburgh (1978) a single hot spot event can influence an area of the crust of the order of 100,000 km^2. At the present time there are about 100 hot spot regions influencing almost 7% of the surface of the planet. The geosphere interaction of hot spots have been inadequately studied. There must be massive water cooling events and where the process is associated with continental crust (the Deccan of India, 500,000 km^2, about 1 km^3 of basalt a^{-1}, the Parana of Brazil), there is even the possibility of perturbation of the chemistry of the atmosphere by oxygen absorption with the reduced materials of the mantle. For example, the present photosynthetic oxygen flux into the the atmosphere is about 4×10^{17} g a^{-1}, while a km^3 of fresh mantle basalt could absorb 3×10^{13} g of oxygen. Massive eruptive events could influence injection of HF, HCl, CO_2 ... into the atmosphere influencing the greenhouse or the ozone layer (Fyfe, 1990).

It is interesting to reflect on the metamorphic record of the fundamental tectonic processes. Subduction zones of modern type produce low T, high P, eclogite and blue schists frequently associated with serpentine diapiric structures. Eclogites could be forming in the root zones of the Himalayas but not serpentine or blue schists. Eclogites could be forming in the thick roots of the Andes (Beck *et al.* 1996) but no blue schists. And with massive thickening of crust by hot spots again eclogite but not blue schists (cf. the model of the Williston Basin of Canada, Fowler and Nisbet, 1985). Almost certainly each type of high pressure metamorphics will carry an isotopic and trace element signature of the precursor materials. Seafloor hydro-thermally cooled mafics should show the interactions with sea water oxygen, hydrogen, helium, strontium, potassium and even halogens. Rock types like massive anorthosites (Fyfe, 1993)

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should carry the record of underplating processes.

Earlier Regimes : There are many diverse views on the tectonics on the early planet. I think the situation is well stated by McCall (1996) speaking of the western Slave Province. "This fragment of the oldest preserved crust is very small, and this illustrates the problem that in the case of the earliest Precambrian, geologist are working on small fragments of the ancient cratons, the rest having been recycled. The Earth processes of subduction and collision act to minimize the area of ancient geological rocks left to us". I am always reminded of words from one of my mentors, F. J. Turner of New Zealand and Berkeley, "never write about what you have not seen—we only see what we are looking for !" When I reflect on my experience in the Proterozoic, I have no problem using models from modern tectonics. But with the Archaean I have problems. The classic work of McGregor (1951) in the Zimbabwe craton and the famous satellite picture of the Pilbara, Australia, have forced many to think of other models. Modern plate tectonics, except for the hot spots, shows us structures, convection, on the multi-thousand km scale. The scales of Archaean magmatism and metamorphism appear on much smaller scale. Is this only because the sample is too small ? And we must never forget that almost half the present Earth's crust will not be here in 200 million years !

In the Archaean there are massive thrust structures, strike slips, super plumes, and hints at ocean ridges and analogies with modern plate tectonics. Are there true ophiolite complexes (cf. Cyprus, Oman, New Foundland) in the Archaean ? Are there sheeted dyke complexes (cf. MacLachlan and Helmstaedt, 1995). I recently spoke to Robert Hargreaves of Princeton and asked him if he had ever seen a Cyprus in the Archaean, the answer was no !

One thing is certain from the laws of fluid convection (Elder, 1976). If the system is more energetic it will have more vigorous but smaller convection cells and more chaos. Recent work (Kerr, 1996b) points towards a more viscous, stiffer, deep mantle. Minarik *et al.* (1996) discuss the separation of core-forming melts (metals, metal sulphides) in the deep mantle. Their conclusion is that to rapidly separate the core, there must have been very substantial partial melting of the system. Given such ideas, the early earth must have been very hot. Recently Kroner and Layer (1992) have written on essentially a hot spot model from the Archaean (cf. Fyfe, 1974). Hot spots, crust of all types submarine, would explain the great metal resource potential of the Archaean.

There is rapid development of ideas. Buick *et al.* (1995) have summarized recent ideas on the 3.5 billion year ago emergent continental crust of the Pilbara craton Australia. They indicate the evidence for a considerable volume of very old continental crust. They also suggest the amount of such crust above sea level was negligible. Eriksson *et al.* (1994) have summarized observations on Archaean greenstone belt sedimentology, with many analogues of more modern systems. Lucas *et at.* (1996) show from the proterozoic Flin Flon Belt of Canada, great similarities with modern systems. Pearson *et al.* 1995) describe Archaean eclogites. Der-Chuen and

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Halliday (1995) describe evidence for very rapid core formation which implies very rapid early heating of the planet.

Abundant sedimentary talc in the Archaean (Costa et al, 1980) perhaps suggests warmer oceans in the Archaean which were dominated by hydrothermal systems (Fyfe et al. 1979). I was intrigued recently by a paper from Rudnick (1995) who suggest "that there may have been a different mode of continental crust generation in Archaean times, and may point to delamination of the lower crust as an important recycling process". Such a model support hot spot underplating (Fyfe, 1993). Vervoort *et al.* (1996) have challenged some of the isotopic wisdom. In general, there is uncertainty about Archaean tectonics regimes which is exactly as we would anticipate from a more energetic planet. It seems the same is true for Venus (Kaula, 1995). It is also interesting to note the recent work of Endress et al. (1996) who have stressed the evidence for $CO_2 - H_2O$ alteration with early, solar-nebular condensates. The earth may have had a very interesting fluid system during its formation.

Discussion continues on the nature of the early atmosphere. Thus Rye *et al.* (1995) using data from fossil soils suggest that greenhouse gases other than CO_2 may have been important in keeping the early Earth warm and suggest that methane may have been more significant. But it should be noted that there is another important greenhouse gas, water. If oceans were a little warmer, and there was more water cooling of the surface, this could be significant.

It is also clear that while tectonics were more complicated, it is probable that the early Sun was also more complicated. Thus Baliunas *et al.* (1990) have shown that young stars similar to our sun show much more chaotic "star spot" cycles. And I was intrigued by recent observations of Renzini *et al.* (1995) of ultraviolet flares in the galaxy with a luminosity one million times our Sun. I am reminded by the classic paper of Berkner and Marshall (1965) suggesting that our first oxygen may have come from the reaction of solar u. v. with water, CO_2 etc. and the suggestion that the atmosphere was not so very different. Similar views based on some ancient sedimentary regimes have been suggested by Kimberley and Dimroth (1976). But for certain, early Earth was a little chaotic which made things difficult for complex species like us. Finally, Harder and Christensen (1996) have analyzed the factors behind volcanic evolution on Mars, from chaotic early patterns to the more recent one-plume system. Perhaps this suggests our future.

High Temperature Gas Phase Transport: Recent work on metal transport in near-surface volcanic systems (Pac Rim Proceedings, 1995) and in granulite facies metamorphics show the power of very high-T fluids in metal transport. As work in volcanic terrains shows, gas phases may be rich in CO_2 amd CO, halogen acids, etc. Fluid inclusion studies on granulites also show high concentraions of CO_2 as would be expected in carbonate-bearing high-T metamorphic and magma underplate regimes.

Experimental studies show that metal like gold and platinum and nickel are readily transported in a CO_2-CO gas phase, (Puddephatt *et al.* 1989). And if a CO-bearing fluid is cooled, the reaction $2CO \rightarrow C$

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(graphite or diamond) + CO_2 will occur. It has been frequently noted that some deep crustal regimes have anomalously high electrical conductivities. Surface chemistry studies on some granulites (Frost *et al.* 1989; Mareschall *et al.* 1992) have shown grain boundaries covered with ultra-thin films of graphite. There is great need to use the new surface analysis techniques, like ESCA, Auger spectroscopy, to search for the tracks of fluids involved in such chemical transport processes.

The Biosphere : Very recently there has been increasing interest in biosphere influences on Earth chemistry and resources. First, there is little doubt that there is evidence for micro-organisms in the most ancient rocks suitable for preserving such species (Mooers and Redfield, 1996). We tend to forget the scale of the living biomass today. Thus, on the Earth's surface environments we have over 1000 km^3 of living matter and three times amount in dead matter. Abelson (1957) indicated that at the present rate of bio-carbon cycling, if integrated over geologic time, the total mass of living cells would be similar to the mass of the earth. And given the inorganics in average living matter, Fyfe (1986b) suggested that it was possible that every potassium atom in the planet had spent part of its residence in a living cell. When one considers the vast array of bio-essential elements (Mertz, 1981) including interesting species like Mo, Cu, Zn, Fe, V ... it is no surprise that living species profoundly influence (often control) the details of atmosphere, hydrosphere, soil, sediment chemistry. Time after time, the near surface weathering processes are mediated by micro-organisms. We have recently been working on such CO_2 fixation processes in Hawaiian basalts opening up the possibility of deep sub-surface disposal of CO_2.

But perhaps the most spectacular recent advances have come from studies of the deep biosphere, in part stimulated by interest in potential bio-corrosion of nuclear waste containers at depth. Recently Pedersen (1993) has reviewed our present knowledge with the record observation of colonies at over 4 km depth at 110°C (Zoback and Emmerman, 1993; Ekendahl, 1996). Micro-organisms are prolific from the ultra-saline lakes of Antarctica, to the deep oil gas fields of the North Sea (Stretter *et al.* 1994). Micro-organisms play a profound role in the transport and fixation of a host of trace elements, influence the state of the C-S systems, all redox systems, and often lead to the formation of ore deposits (Fyfe, 1986b).

The potential for the use of micro-organism in various types of our resource technologies (deep water cleaning, metal extraction, methane production, CO_2 fixation) is impressive. And when atmospheric states are analyzed on the basis of the state of soils and sediments, the role of micro-organism must be considered (for example the common presence of magnetotatic bacteria precipitating Fe_3O_4 in soils or sediments clearly shows that our present atmosphere has little oxygen).

Conclusion : One of the greatest challenges facing all involved in Earth System Science, is the precise quantification of all processes influencing the dynamics of the chemistry of the outer geospheres and the relations to the life support systems of Homo sapiens. Given population growth and future resource needs, models of geochemical

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processes in crust of all ages must be improved. Recent work has shown the vast importance of geosphere mixing, including the biosphere in crustal processes to depths of several kilometres, processes which have probably operated for all recorded time.

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Numerical solution of a phase boundary problem using Fourier Series

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Abstract : The determination of phase boundary due to perturbation in basal heat flux and plume temperature has been discussed for a one-dimensional lithosphere thinning problem. The nonlinear problem is solved using a Fourier series method and stiffness arising in the system is removed by Melamed method. Various heat flux are chosen to demonstrate the effect on the moving front with and without plume temperature and time taken by the moving phase boundary is calculated for different cases of heat variation.

(**Keywords** : plume temperature/heat flux perturbation/ phase boundary)

Intoduction : A significant quantum of intra plate volcanic activity is related to hot spots, however some intra continental activities may clearly be associated with extensional tectonics and rifting, e.g., East African Rift, the Rhine Graben Rift and the rift at Basin and Range province (M. Wilson). Such continental rifting, whether active or passive is considered to be areas of localized lithoshperic extension characterized by central depression, uplift of the flanks and thinning of underlying crust. These continental rift zones are characterized by anomalously high heat flow, long wave length Bouguer anomalies and anomalous seismic structures (Gass 1978, Zorin 1981). Altogether these observations point to thinned lithosphere beneath continental rift structures.

Modern theories of tectono-thermal, thermo-mechanical and geochemical aspects of rift formation propose the existence of a mantle hot spot beneath the lithosphere. To model the lithosphere thinning, researchers in recent years have considered it as a phase boundary problem or Stefan problem (Manglik 1992, Gliko and Mareschall 1989). The movement of boundary is associated with determination of boundary as a function of time and space, which involves the non-linearity in the resulting system of equations.

Non-linearity involved in such system makes it difficult to solve by analytical methods such as Integral equation method (Mareschall J. C. 1977), Enthalpy method (Eyres *et al.* 1960) and Green's function approach (Nakiboglu 1978) etc. Various numerical schemes have also been used to solve these problems (Crank 1994, Manglik 1992, Gliko 1985 etc.). Manglik *et al.* (1992) used a modified Fourier series method to solve the lithosphere thinning problem. In the

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lithosphere thinning problem (Crough and Thompson 1976, Spohn and Schubert 1985) a set of coupled differential equations occur with or without phase changes. The unknown function present in the partial differential equation is expressed in an infinite number of orthogonal functions (Canuto 1988). The orthogonality of functions is used further in solving the differential equations. Fourier series coefficients occurring in the unknown functions can be evaluated for an optimal level.

In this paper an additional condition on the boundary is used which takes into account the effect of a term which arises due to consideration of placement of a plume beneath the lithosphere. The condition on moving front used by Manglik *et al.* (1992) may be considered as a special case of this additional condition. In the absence of actual equilibrium state of domain the choice of actual heat flux variation becomes critical. So some general type of heat flux variation are chosen to evaluate and analyze effect of proposed boundary condition. Melamed method (1958) has been used to take care of stiffness occurring in the differential equation by the use of Fourier series used for changing non-linear system into ordinary system of differential equations.

The emplacement of plume clearly shows that in all cases of different type of heat variation time, taken for attaining the stability position by the moving boundary increases to a large extent.

Mathematical Model : Perturbed normalized heat conduction equation describing the temperature in the lithosphere satisfies :

$$\frac{\partial \theta}{\partial t} = \frac{\partial^2 \theta}{\partial z^2} \qquad 0 \le z \le \xi(t) \tag{1}$$

where $\theta = u(z, t) - u_0(z)$

The condition on the moving front is given by

$$\frac{\partial \theta}{\partial t} + \frac{\partial u_0}{\partial z} - R\,q(t) = (\alpha + U_{pm})\frac{\partial \xi}{\partial t} + \beta\,\xi(t)\frac{\partial \xi(t)}{\partial t} \tag{2}$$

where

$\theta(0, t) = 0 = \theta(z, 0)$,

$\theta(\xi(t), t) = \phi(\xi(t))$,

$\xi(0) = 1$, and $Upm = Up - Um$

Here, $u(z, t)$ is thermal distribution normalized by T_m, which is the solidus temperature. $u_0\ z$ is the initial temperature distribution in lithosphere (normalized to T_m), U_p is normalized plume temperature, U_m is base temperature and z, the space coordinate considered positively down-wards and is normalized by l_0, l_0 being lithoshperic thickness. The time t is normalized by τ_0, which denotes character- istic time ($\tau_0 = l_0^2/k$). α (Stefan number $\alpha = \lambda/cT_m$) is normalized by T_m. λ is latent heat of fusion and c is heat capacity. $\beta = \Delta\rho g l_0/(\rho_1\ cT_m))$ is coefficient occurring due to density changes, with $\Delta\rho = (\rho_1 - \rho_a)$.

Here ρ_1 is density of lithoshpere and ρ_a is density of asthenosphere. g is acceleration due to gravity and a is slope of Clapeyron curve. R ($l_0\ Q_0/k\ T_0$) is the parameter describing nature of initial temperature profile. $q(t)$ is heat flux normalized by Q_0, (Q_0 is initial

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steady state value of heat flow).

Using the transformation

$$V(z,t) = \theta(z,t) - \frac{z}{\xi(t)}\,\phi(\xi(t)) \qquad (3)$$

initial condition becomes

$$V(z,t) = 0,\ V(\xi(t), t) = 0$$

Expressing $V(z, t)$ as Fourier series, we have

$$V(z,t) = \frac{2}{\xi(t)} \sum_{k=1}^{k=\infty} A_k t \sin\left(\frac{\pi k z}{\xi(t)}\right) \qquad (4)$$

Thus, the equation (1) reduces to

$$\frac{\partial V}{\partial t} = \frac{\partial^2 V}{\partial t^2} + \frac{z}{\xi^2}\,\phi\,\frac{\partial \xi}{\partial t} - z\phi'\,\frac{\partial \xi}{\partial t} \qquad (5)$$

Applying the orthogonality and integrating we get the following system

$$\frac{dA_n(t)}{dt} = -\left(\frac{n\pi}{\xi(t)}\right)^2 A_n(t) - \frac{2n\,\partial\xi}{\xi(t)\,\partial t} \sum A_k(t) p_{nk} - \frac{(-1)^n (R-a)}{n\pi}\,\frac{\partial \xi}{\partial t} + \frac{A_n(t)}{\xi(t)}\,\frac{\partial \xi(t)}{\partial t} \qquad (6)$$

where

$$p_{nk} = \begin{cases} (-1)^{n+k}\left(k/\left(n^2 - k^2\right)\right) & n \neq k \\ -1/4n & n = k \end{cases}$$

Similarly the condition on the moving front is obtained as

$$\frac{d\xi}{dt} = \frac{1}{\alpha + Upm + \beta\,\xi(t))} \left\{ \frac{2^n}{\xi^2} \sum (-1)^k A_k(t)\,k + \frac{(R-a)(1-\xi(t))}{\xi(t)} + R(1 - q(t)) \right\} \qquad (7)$$

Equations (6) and (7) constitute a non-linear boundary value problem which can be solved iteratively by a finite difference scheme. The values of parameters can be calculated and then substituted in equations (3) and (4) to obtain the movement of phase boundary.

Computational Details : The transformed system of equations (6, 7), which give the phase boundary movement or temperature distribution includes infinite set of orthogonal functions and therefore, the same number of Fourier coefficients. A finite- difference scheme proposed by Melamed (1958) is used and in computation a finite number of Fourier coefficients are considered to describe the movement. In our computations we have taken $N = 20$ in all the three cases considered here. These numbers of Fourier coefficients are sufficiently large and adequate because the relative error reduces from 6.2% to 0.4% when Fourier coefficients are increased from 6 to 18 (Manglik 1992). The values of different input parameters i.e. R (the parameter describing initial temperature profile), α (the Stefan number) and β (the parameter describing the contribution of density changes) can be calculated from their formulae given in the

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modelling section. But we have taken these values of R, α and β as 0.6, 0.027 and 0.00077 respectively. $\alpha = 0.0$ denotes the situation of subsolidus model and the value of α different from zero implies that the asthenosphere is at the solidus and there is some partial melting. $\beta = 0$ takes into account the fact that there are no density changes in the two phases when the system perturbed with time.

Before discussing our results for the three cases, it is necessary to discuss the values of plume temperature and the temperature at the base of lithosphere which must be provided to follow the upward movement of lithosphere base. Although the lithosphere-asthenosphere boundary cannot be sharp even then the highly sensitive temperature dependence of viscosity of mantle suggests that it can be best identified with a particular isotherm or fraction of melting temperature. Again since, there is large uncertainty in the determination of various parameters in the mantle, most researchers generally use a temperature of 1000°C as the solidus (Oxburg and Turcoutte, 1978 and Schubert 1979). Therefore, this values is chosen for the base of lithosphere. Two values of plume temperatures are taken as 1100°C and 1200°C as these are appropriate for the

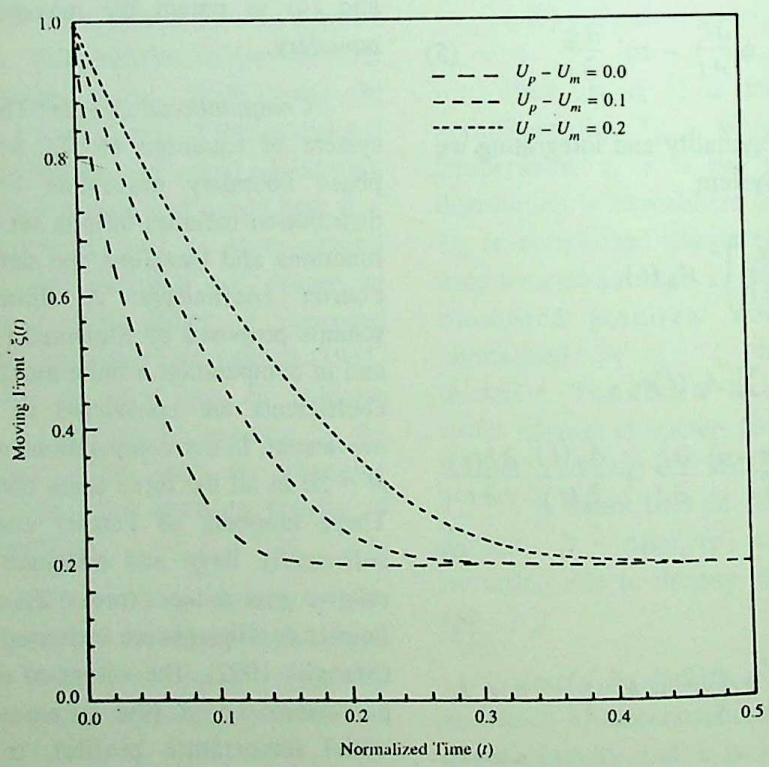

Fig. 1–Response of moving phase boundary with time due to step-wise heat flux ($q = 3.0$). The moving front is shown for $\alpha = 0.027$, $\beta = .00077$ and $R = 0.6$.

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analysis and are in general agreement with those available in literature. In all three cases $U_p - U_m = 0.0$ show the case of not implementing the plume temper- ature. The other two types show the effect of two different cases of plume temperature 1100°C and 1200°C. In normalized terms they are taken as $U_p = 1.1$ and 1.2 and U_m which is the base temperature as 1.0. We now discuss and compare them with the results obtained by Manglik (1992).

Case 1 : In the first case the nature of moving front is described, and heat flux given as

$$q = q_0$$

We have taken $q = 3.0$. The movement of phase boundary for this is shown in Fig.1.

The temperature distribution is not shown for the sake of convenience. When U_p is taken equal to Um for $\alpha = 0.027$ the boundary slowly moves upwards and acquires a constant level at 0.22 unit of time. During this time a significant amount of thinning is found i.e. 80% for a short time (0.22 unit). This case is equivalent to the case-1 considered by Manglik (1992) for $\alpha = 0.1$ and $R = 1.0$. We have chosen the values of R as 0.6. When we assume the existence of plume temperature, the thinning time increases to a considerable amount. Same amount of thinning found in previous case occurs at 0.36 unit of time when we take $U_p - U_m = 0.1$. When $U_p - U_m = 0.2$ i.e., a difference of 200°C is considered between plume temperature and base temperature, then 80% thinning of litho- sphere requires 0.48 unit of time.

Therefore, the time taken by a moving front to stabilize is increased by 0.14 unit of time for a difference of 100°C between U_p and U_m and 0.26 units of time for a difference of 200°C between U_p and U_m from the case originally taken by Manglik (1992). Thus the moving phase boundary takes steady state position over a large period if time when plume emplacement is taken under consideration.

Case 2 : We now consider periodically decreasing type of heat variation to demonstrate the effect on the moving front. Such type of function may match real situations.

The function describing heat flux is defined as :

$$q = C_0 \exp(-t/C_1) + C_2 \exp(-C_3 t) \sin(k\pi t)$$

where

C_0, C_1, C_2, C_3 and k are arbitrarily chosen constants, but they are so chosen that the stability and smoothness of boundary are controlled and match physical situations.

C_0 is taken as 3.0 to consider the effect of large heat flow and C_1, C_2 and C_3 are chosen as 2.0, 0.5 and 1.0, respectively.

To consider the changes due to low frequency k is taken as 10.0 (Fig. 2). When U_p is equal to U_m , and the oscillatory boundary rapidly moves upwards in very small time i.e., 0.1 unit and slowly oscillates after this time but does not attain stability. However, the oscillation reduces for large value of time. When $U_p - U_m$ is taken as 0.1 i.e., a

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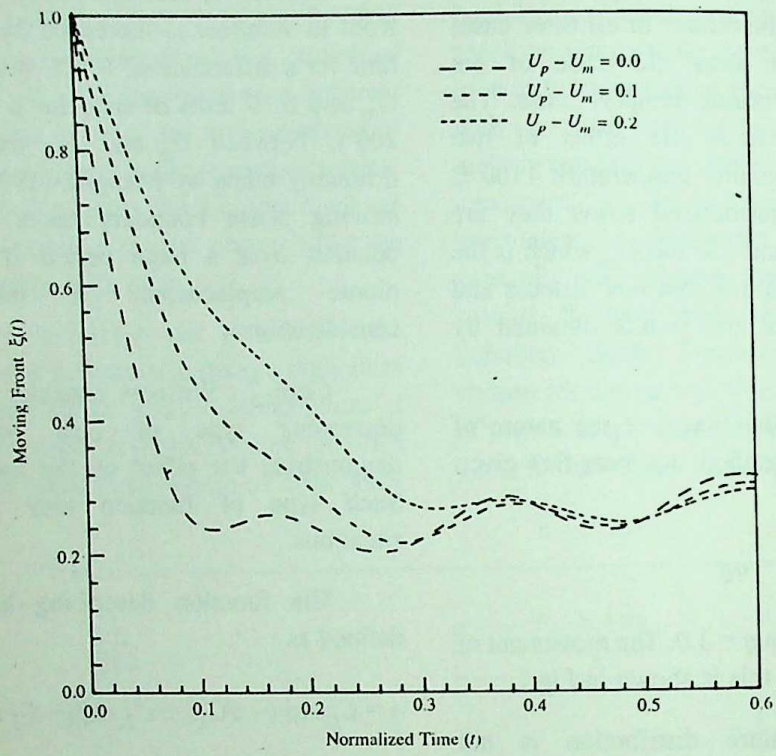

Fig. 2–The moving front for the Periodically decreasing type of heat variation ($q = 3.0 \times e^{(-t/2.0)} + 0.5 \times e^{(-t)} \sin(10\pi t)$ are shown for same values of α, β and R as in Fig. 1

temperature difference of 100°C, the boundary movement becomes very slow and tries to attain a constant level at about 0.40 units of time though it has acquired a constant oscillation level equal to 0.3 unit of time. When $U_p - U_m$ is equal to 0.2 then as before the boundary movement becomes much slower and the moving front stabilizes at around 0.48 units of time.

Case 3 : Another heat flux is considered in the third case, where

$$q = C_0 \log (C_1 + C_2 t) + C_3 \exp (- C_4 t) (k\pi t)$$

Here

$$C_0 = 1.0, C_1 = 1.0,$$

$$C_2 = 10.0, C_3 = 0.5,$$

$$C_4 = 1.0 \text{ and } k = 10.0.$$

This function also shows the same results as the previous function but here the boundary movement becomes much slow and it stabilizes after 0.6 units of time. (Fig. 3)

Conclusion : A number of other important geological and geophysical problems involve moving boundaries such as

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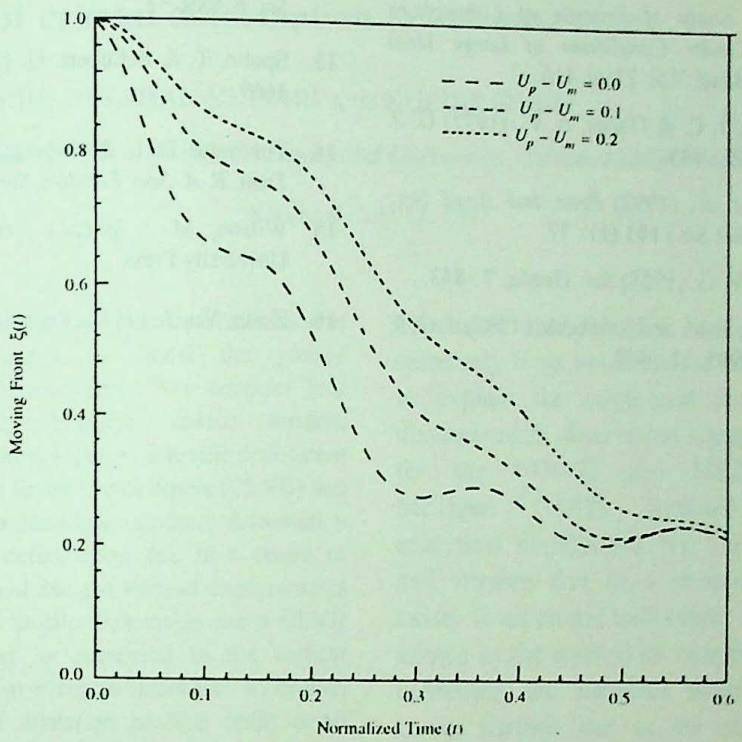

Fig. 3–A more general type of heat variation is taken in this case and the response of moving front are shown. (q = 1.0* log (1.0 + 10t) + 0.5* exp (-t)* sin (10.πt)

solidification of igneous intrusives, erosion and sedimentation which can be investigated/ modelled using moving boundary formulation. Though the non-linearity involved in the system of various tectono-thermal and thermo mechanical problems makes the solution of posed problem difficult even then Fourier series method as given above can be used to solve phase boundary problems efficiently.

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Modelling of crustal deformation in volcanic areas

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Abstract : Mogi (1958) used a centre of dilatation in an elastic half-space to model the ground deformation in volcanic areas. We consider four additional axially-symmetric source models, namely, a single force, a dipole, a tensile dislocation and a compensated linear vector dipole (CLVD) and compare the corresponding surface deformation with the surface deformation due to a centre of dilatation. It is found that the vertical displacements due to a dipole, a tensile dislocation and a CLVD decay much faster as compared to the vertical displacement due to a centre dilatation. Moreover, while a centre of dilatation predicts uplift at all epicentral distances, a dispole of a CLVD predicts subsidence after a certain epicentral distance.

(**Kewwords** : ground deformation modelling/volcanic areas)

Introduction : Mogi (1958) used a centre of dilatation in an elastic half-space to interpret the ground deformation produced in volcanic areas. This model is often called Mogi's model after him and has been used very extensively since then. Dieterich and Decker (1975) used a finite element method with different shapes for the magma chamber to model surface deformation associated with volcanism. Bianchi *et al.* (1987) also used a finite element method to calculate the surface deformation, assuming axial symmetry about the vertical axis through the caldera centre. They concluded that Mogi's model requires an extremely large value for the pressure increase to explain the large and localized surface displacements observed at Campi Flegrei, Italy for the 1970-72 and 1982-1984 events. McTigue (1987) obtained approximate analytical expressions for the displacements and stresses due to a pressurized spherical cavity in an elastic half-space. In this method, known as the method of images, the boundary conditions are statisfied alternatively at the cavity surface and at the plane boundary. McTigue concluded that the effect of the finite radius of the cavity on the surface uplift is quite weak.

Bonafede *et al.* (1986) obtained an analytical solution for the displacement field due to a centre of dilatation in a viscoelastic half-space. The results obtained are applied to the volcanic area of Campi Flegrei. It is shown that the consideration of viscoelasticity allows the same deformation to take place with much lower pressure values in the magma chamber than are required by purely elastic models. Davis (1983) advocated the use of a tensile dislocation in a half-space for interpreting naturally induced hydrofracture of the earth's crust such as the magmatic intrusion into sills and dikes in volcanic zones, including the

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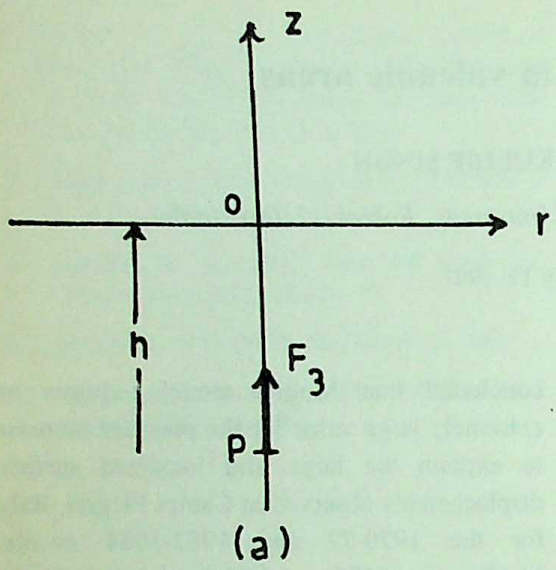


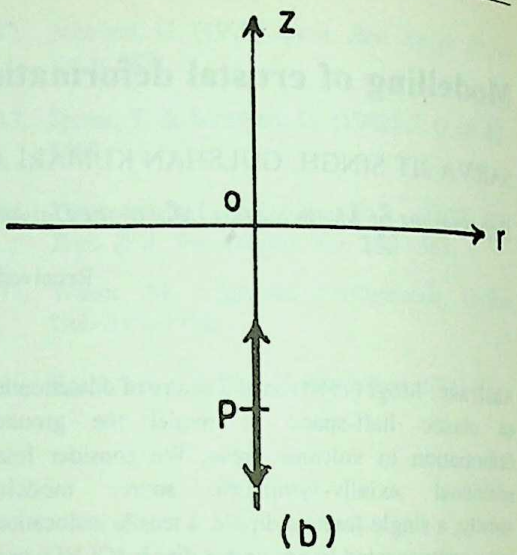
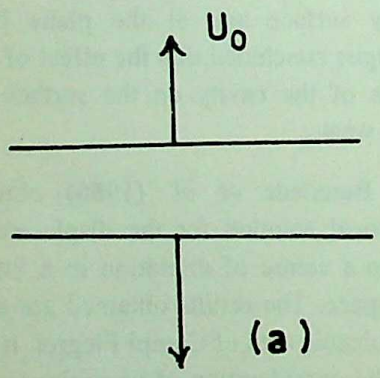


Figure 1– (a) Vertical force of magnitude F_3 placed at the point P of a uniform half-space at a depth, h.

(b) Vertical dipole.



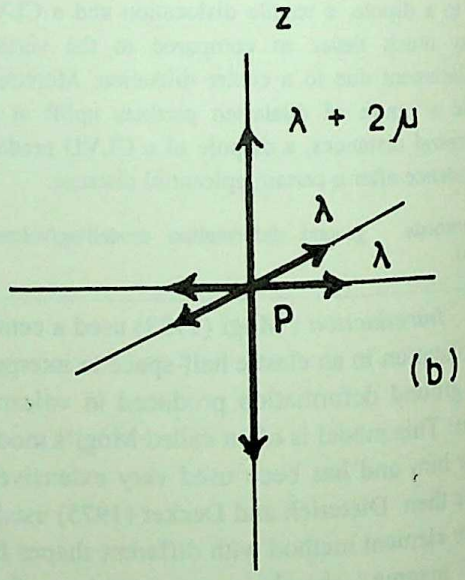


Figure 2– (a) A tensile dislocation of magnitude U_0 on a horizontal plane.

(b) Equivalent body force.

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mid-ocean ridges, volcanic rift zones and continental rifts. Okada and Yamamoto (1991) constructed a dislocation model for the 1989 seismo-volcanic activity off Ito, central Japan, based on crustal movement data and seismic data. This model consists of two tensile faults corresponding to magma intrusions in May and July 1989, and a right-lateral reverse fault representing the largest seismic event (M 5.5) of July 9, 1989.

We consider four additional axially symmetric sources, namely, a vertical force, a vertical dipole, a tensile dislocation on a horizontal fault and a compensated linear vector dipole (CLVD) in an elastic half-space to model the ground deformation in volcanic areas. The displacement and strain fields due to these four sources are compared with the corresponding fields due to a centre of dilatation.

There is a fundamental difference between the single force source model and the remaining four source models considered in this paper. While the single force is a unipolar source, the remaining four source are dipolar and the corresponding equivalent force systems have zero total force and zero total torque. Takei and Kumazawa (1994) have given a theoretical justification for the physical existence of sigle-force and torque components from indigenous earthquake sources. According to them, the most promising indigenous events for detecting and identifying single forces and torques are those beneath volcanic regions.

Theory : The problem of the static deformation due to a point source buried in an elastic half-space has been discussed extensively in literature (Mindlin 1936, Mindlin and Cheng 1950, Maruyama 1964, Okada 1985, Singh and Singh 1989). The expressions for the surface displacements for various sources given below have been obtained from Singh and Singh (1989). We assume that the half- space occupies the region $z = 0$ the plane $z = 0$, is stress-free and the point source is located at a depth h below the free surface. We use a cylindrical co-oridnate system (r, e, z) with the z-axis vertically upwards.

Vertical Force : For a vertical point force of magnitude F_3 (Fig. 1a), the radial and vertical components of the displacements and strain at the surface of the half-space ($z = 0$) are given by :

$$u_r = \frac{F_3 r}{4\pi \mu R}\left(\frac{h}{R^2} + \frac{1-2\sigma}{R+h}\right), \tag{1}$$

$$u_z = \frac{F_3}{4\pi \mu R}\left(2(1-\sigma) + \frac{h^2}{R^2}\right), \tag{2}$$

$$e_{rr} = \frac{F_3}{4\pi \mu R}\left[\frac{h}{R^2}\left(1 - \frac{3r^2}{R^2}\right) + (1-2\sigma)\left(\frac{h}{R^2} - \frac{1}{R+h}\right)\right], \tag{3}$$

$$e_{zz} = \frac{\sigma F_3 h}{4\pi \mu (1-\sigma) R^3}\left(2\sigma - \frac{3h^2}{R^2}\right), \tag{4}$$

where μ is the rigidity, σ the Poisson's ratio and

$$R^2 = r^2 + h^2. \tag{5}$$

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Vertical Dipole : For a vertical dipole of moment F_{33} (Fig. 1b), the surface deformation is given by :

$$u_r = \frac{F_{33}\, r}{4\pi\, \mu R^3}\left(\frac{3h^2}{R^2} - 2\sigma\right), \tag{6}$$

$$u_z = \left(\frac{h}{r}\right) u_r, \tag{7}$$

$$e_{rr} = \frac{F_{33}}{4\pi\, \mu R^3}\left[3h^2\left(\frac{1}{R^2} - \frac{\sigma\, r^2}{R^4}\right) - 2\sigma\left(1 - \frac{3r^2}{R^2}\right)\right], \tag{8}$$

$$e_{zz} = -\frac{\sigma F_{33}}{4\pi\, \mu(1-\sigma)R^3} \times \left[2\sigma - \frac{3(3+2\sigma)h^2}{R^2} + \frac{15h^4}{R^4}\right]. \tag{9}$$

Centre of Dilatation : A centre of dilatation is equivalent to three equal mutually orthogonal dipoles. If the moment of each of these dipoles is M_0, the surface deformation is given by

$$u_r = \frac{(1-2\sigma)\, M_0}{2\pi\, \mu}\left(\frac{r}{R^3}\right), \tag{10}$$

$$u_z = \left(\frac{h}{r}\right) u_r, \tag{11}$$

$$e_{rr} = \frac{(1-2\sigma)\, M_0}{2\pi\, \mu R^3}\left(1 - \frac{3r^2}{R^2}\right), \tag{12}$$

$$e_{zz} = \frac{\sigma(1-2\sigma)\, M_0}{2\pi\, \mu(1-\sigma)R^3}\left(1 - \frac{3h^2}{R^2}\right). \tag{13}$$

Tensile Dislocation : A tensile dislocation U_0 (Fig. 2a) on a horizontal planer element of area dS is equivalent to a vertical dipole of moment $(\lambda + 2\mu)U_0 dS$ plus two mutually orthogonal horizontal dipoles of moment $\lambda U_0 dS$ each (Fig. 2b, Ben-Menahem and Singh 1981). The corresponding surface deformation is found to be

$$u_r = \frac{3U_0 dS\, h^2\, r}{2\pi\, R^5}, \tag{14}$$

$$u_z = \left(\frac{h}{r}\right) u_r, \tag{15}$$

$$e_{rr} = \frac{3U_0 dS\, h^2}{2\pi R^5}\left(1 - 5\frac{r^2}{R^2}\right), \tag{16}$$

$$e_{zz} = \frac{3U_0 dS\, h^2}{2\pi\, R^5}\left(3 - 5\frac{h^2}{R^2}\right). \tag{17}$$

Compensated Linear Vector Dipole : A compensated linear vector dipole (Knopoff and Randall 1970) consists of three mutually orthogonal dipoles with moments in the ratio (– 1, –1, 2). If the principal dipole of moment 2M is vertical (Fig. 3), the surface deformation is given by

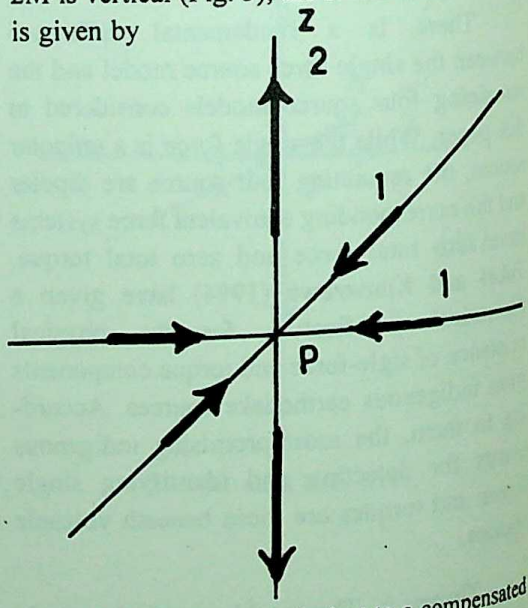

Figure 3– Body forces equivalent to a compensated linear vector dipole.

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$$u_r = \frac{Mr}{4\pi\mu R^3}\left(\frac{9h^2}{R^2} - 2(1+\sigma)\right), \quad (18)$$

$$u_z = \left(\frac{h}{r}\right)u_r, \quad (19)$$

$$e_{rr} = -\frac{M}{4\pi\mu R^3}\left[2(1+\sigma)\left(1-\frac{3r^2}{R^2}\right) \times \frac{9h^2}{R^2}\left(1-\frac{5r^2}{R^2}\right)\right], \quad (20)$$

$$e_{zz} = -\frac{\sigma M}{4\pi\mu(1-\sigma)R^3} \times \left(2(1+\sigma) - 3(11+2\sigma)\frac{h^2}{R^2} + \frac{45h^4}{R^4}\right). \quad (21)$$

Numerical Results : We define dimensionless epicentral distance D, dimensionless radial displacement U and dimensionless vertical displacement (uplift) W by the relations

$$D = \frac{r}{h},\ U = \frac{A}{h}u_r,\ W = \frac{A}{h}u_z,$$

$$E_{11} = A\,e_{rr},\ E_{33} = A\,e_{zz}, \quad (22)$$

where A is a dimensionless constant.

For each source, we choose A in such a manner that $W = 1$ at $r = 0$.

Vertical Force : From equations (1)-(5), we find

$$U = \frac{D}{(3-2\sigma)(1+D^2)^{1/2}} \times \left[\frac{1}{1+D^2} + \frac{1-2\sigma}{1+(1+D^2)^{1/2}}\right], \quad (23)$$

$$W = \frac{1}{(3-2\sigma)(1+D^2)^{1/2}} \times \left[2(1-\sigma) + \frac{1}{1+D^2}\right], \quad (24)$$

$$E_{11} = \frac{1}{(3-2\sigma)(1+D^2)^{1/2}} \times \left[\frac{1-2D^2}{(1+D^2)^2} + (1-2\sigma) \times \left\{\frac{1}{1+D^2} - \frac{1}{1+(1+D^2)^{1/2}}\right\}\right], \quad (25)$$

$$E_{33} = \frac{\sigma}{(3-2\sigma)(1-\sigma)(1+D^2)^{3/2}} \times \left[2\sigma - \frac{3}{1+D^2}\right], \quad (26)$$

$$A = \frac{4\pi\mu h^2}{(3-2\sigma)F_3}. \quad (27)$$

Vertical Dipole : From equations (6)-(9), we have

$$U = \frac{D}{(3-2\sigma)(1+D^2)^{3/2}}\left(\frac{3}{1+D^2} - 2\sigma\right), \quad (28)$$

$$W = U/D, \quad (29)$$

$$E_{11} = \frac{1}{(3-2\sigma)(1+D^2)^{5/2}} \times \left[\frac{3(1-4D^2)}{1+D^2} - 2\sigma\left(1-2D^2\right)\right], \quad (30)$$

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$$E_{33} = -\frac{\sigma}{(3-2\sigma)(1-\sigma)(1+D^2)^{3/2}} \times \left[2\sigma - \frac{3(3+\sigma)}{1+D^2} + \frac{15}{(1+D^2)^2}\right], \quad (31)$$

$$A = \frac{4\pi\mu h^3}{(3-2\sigma)F_{33}}. \quad (32)$$

Centre of Dilatation : From equations (10)-(13), we find

$$U = \frac{D}{(1+D^2)^{3/2}}, \quad (33)$$

$$W = U/D, \quad (34)$$

$$E_{11} = \frac{1-2D^2}{(1+D^2)^{5/2}}, \quad (35)$$

$$E_{33} = \frac{\sigma(D^2-2)}{(1-\sigma)(1+D^2)^{5/2}}, \quad (36)$$

$$A = \frac{2\pi\mu h^3}{(1-2\sigma)M_0}. \quad (37)$$

Tensile Dislocation : From equations (14)-(17), we get

$$U = \frac{D}{(1+D^2)^{5/2}}, \quad (38)$$

$$W = U/D, \quad (39)$$

$$E_{11} = \frac{1-4D^2}{(1+D^2)^{7/2}}, \quad (40)$$

$$E_{33} = \frac{\sigma(3D^2-2)}{(1-\sigma)(1+D^2)^{7/2}}, \quad (41)$$

$$A = \frac{2\pi h^3}{3U_0\, dS}. \quad (42)$$

Compensated Linear Vector Dipole : From equations (18)-(21), we have

$$U = \frac{D}{(7-2\sigma)(1+D^2)^{3/2}}\left[\frac{9}{1+D^2} - 2(1+\sigma)\right] \quad (43)$$

$$W = U/D, \quad (44)$$

$$E_{11} = -\frac{1}{(7-2\sigma)(1+D^2)^{3/2}} \times \left[\frac{2(1+\sigma)(1-2D^2)}{1+D^2} - \frac{9(1-4D^2)}{(1+D^2)^2}\right] \quad (45)$$

$$E_{33} = \frac{\sigma}{(7-2\sigma)(1-\sigma)(1+D^2)^{3/2}} \times \left[2(1+\sigma) - \frac{3(11+2\sigma)}{1+D^2} + \frac{45}{(1+D^2)^2}\right] \quad (46)$$

$$A = \frac{4\pi\mu h^3}{(7-2\sigma)M}. \quad (47)$$

Figure 4 shows the variation of the vertical displacement (uplift) with epicentral distance. For a single force, a centre of dilatation and a tensile dislocation, the vertical displacement is always an uplift. However, from equation (29), we note that, for a dipole the vertical displacement vanishes at

$$D = \left(\frac{3-2\sigma}{2\sigma}\right)^{1/2},$$

which yields $D = 2.24$ for $\sigma = 0.25$.

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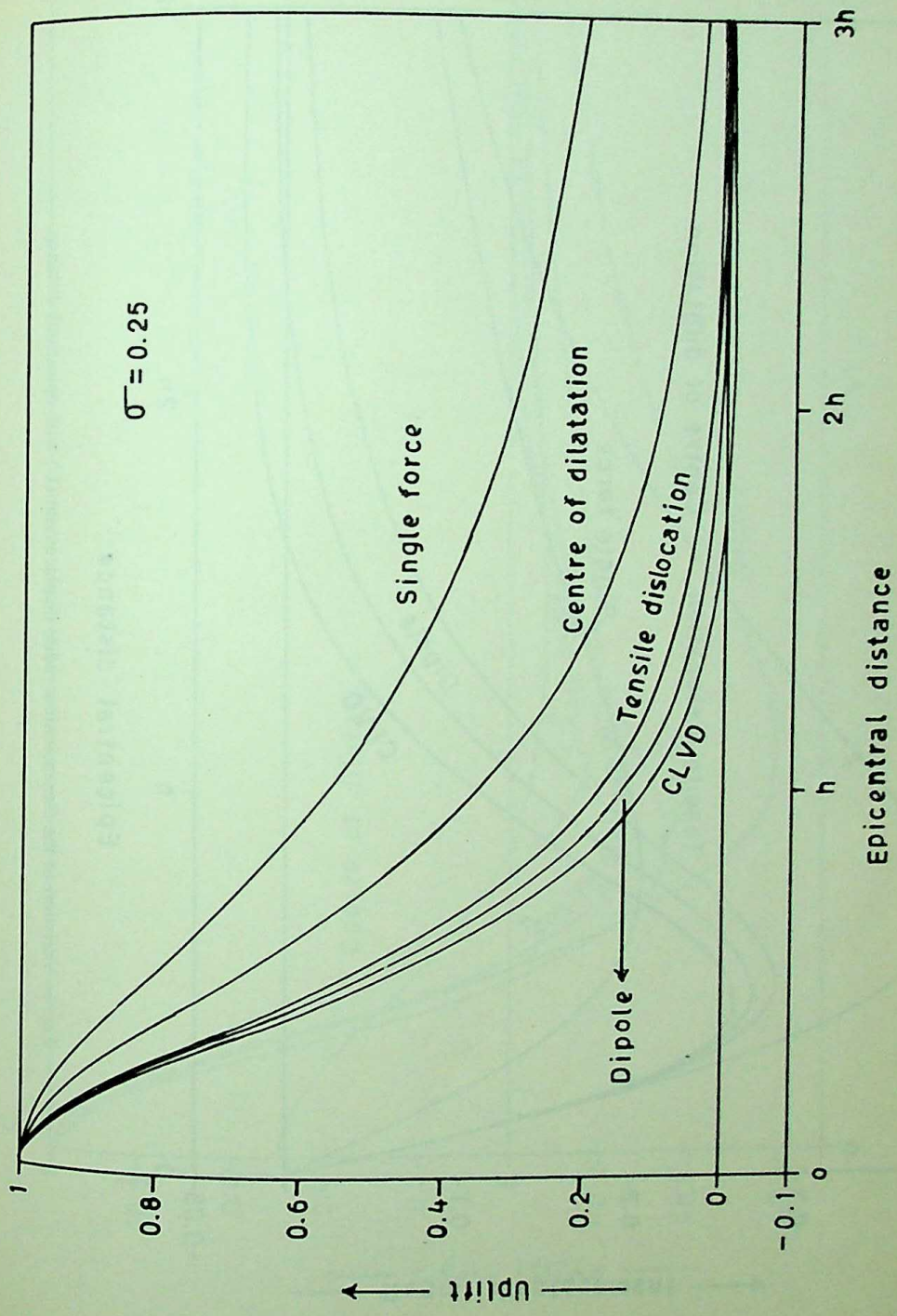

Fig. 4–Variation of the dimensionless vertical displacement (uplift, W) with epicentral distance. For each source, the sources strength is so normalised as to make $W = 1$ at $r = 0$.

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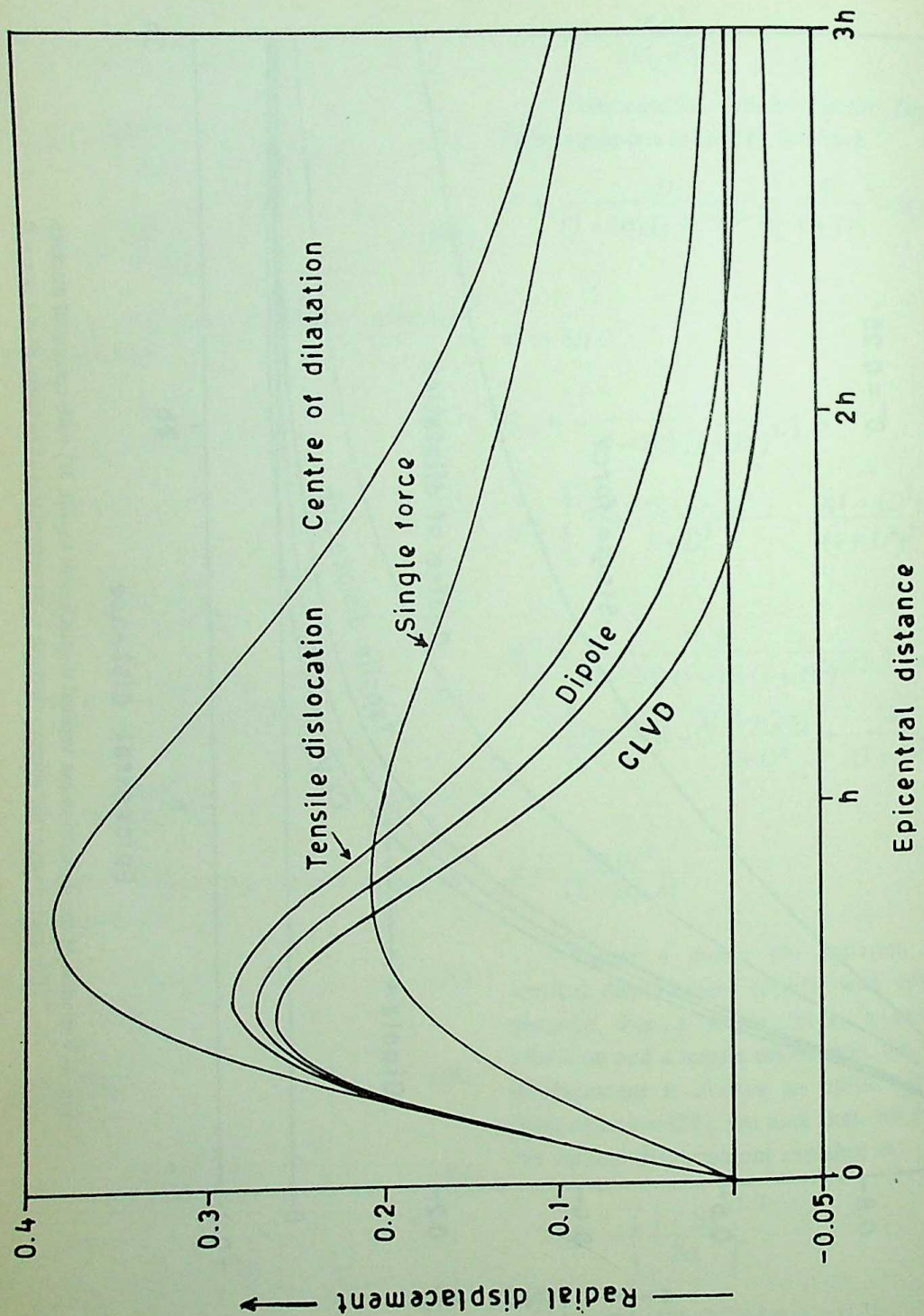

Fig. 5– Variation of the dimensionless radial displacement (U) with epicentral distance.

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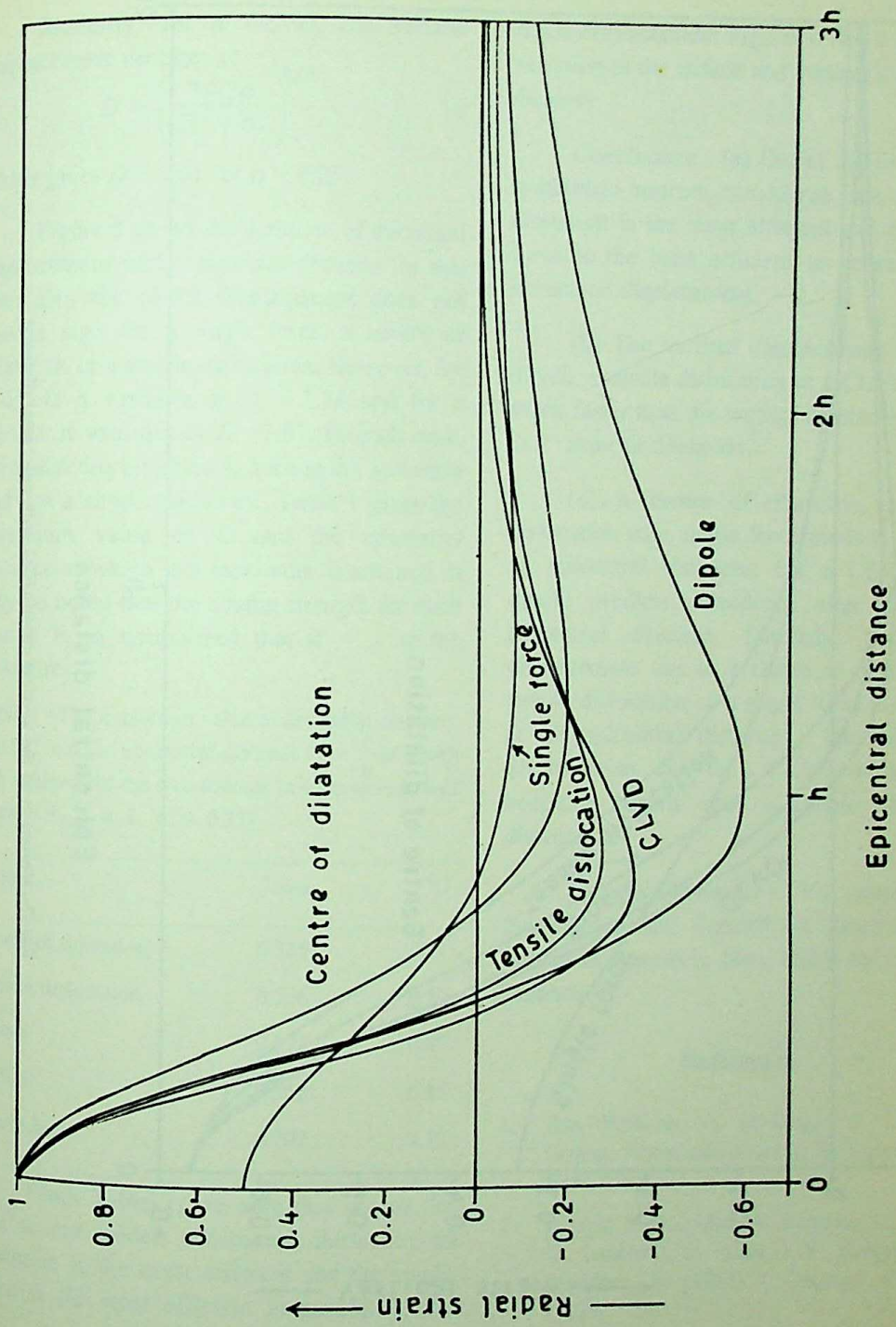

Fig. 6– Variation of the radial strain (E_{11}) with epicentral distance.

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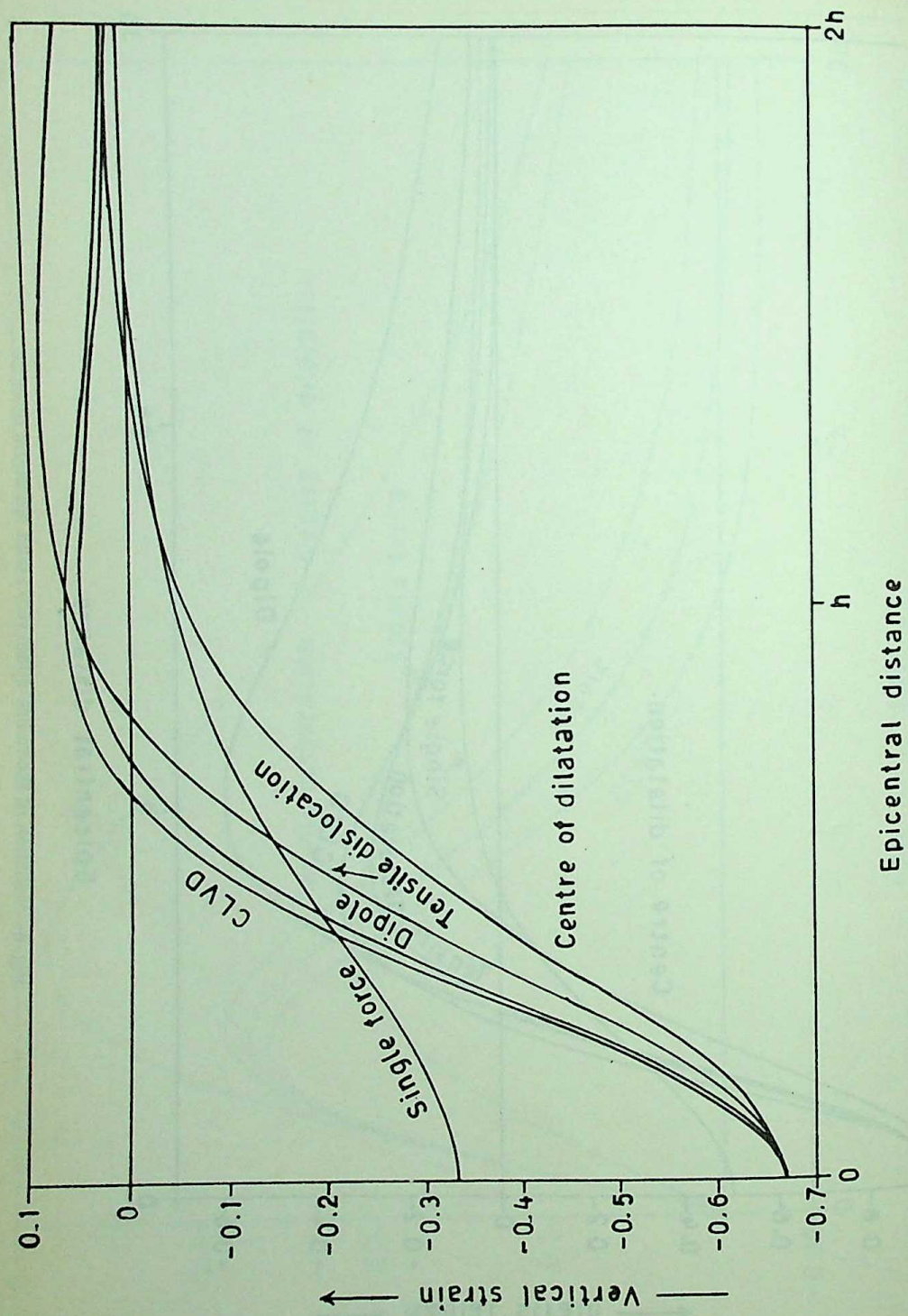

Fig. 7– Variation of the vertical strain (E_{33}) with epicentral distance.

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Similarly, for a CLVD, the vertical displacement vanishes at

$$D = \left(\frac{7 - 2\sigma}{2(1 + \sigma)} \right)^{1/2}$$

which gives $D = 1.61$ for $\sigma = 0.25$.

Figure 5 shows the variation of the radial displacement with epicentral distance. In this case also the radial displacement does not change sign for a single force, a centre of dilatation or a tensile dislocation. However, for a dipole it vanishes at $D = 2.24$ and for a CLVD, it vanishes at $D = 1.61$. In each case, the radial displacement is zero at the epicentre and has a single minimum. Table 1 gives the maximum value of U and the epicentral distance at which this maximum is attained. It may be noted that the source strength for each source is so normalized that $W = 1$ at the epicentre.

Table 1 –The maximum value of the radial displacement U and the epicentral distance $D = \frac{r}{h}$ at which it is attained for the five sources in a Poissonian half space ($W_{max} = 1$, $\sigma = 0.25$)

Source	U_{max}	D
Centre of dilatation	0.385	0.71
Tensile dislocation	0.286	0.50
Dipole	0.273	0.47
CLVD	0.262	0.45
Single force	0.207	0.79

From Table 1, we note that out of the five source models considered, the centre of dilatation is the most efficient and the single force is the least efficient in generating the radial displacement. Figures 6 and 7 depict the variation of the radical and vertical strains with distance.

Conclusions : (a) Out of the five axially symmetric sources considered, the centre of dilatation is the most efficient and the single force is the least efficient in generating the horizontal displacement.

(b) The vertical displacement due to a dipole, a tensile dislocation or a CLVD decays much faster than the vertical displacement due to a centre of dilatation.

(c) A centre of dilatation, a tensile dislocation or a single force predicts uplift at all epicentral distances; but a CLVD or a dipole predicts subsidence after a certain epicentral distance. Similarly, the radial displacement due to a centre of dilatation, a tensile dislocation or a single force is outward at all epicentral distances but the radial displacement due to a CLVD or a dipole becomes inward after a certain epicentral distance.

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The structure of the siang window, its evolution and bearing on the nature of eastern syntaxis of the Himalaya

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Abstract : The allochthonous low grade pre-Tertiary metamorphic rocks underlying the high grade crystalline nappe, override the frontal belt Neogene molasse sediments along Main Boundary Thrust (MBT). In eastern Himalaya, marine Paleogene sediments are only exposed as narrow thrust slivers over wide lateral extent close to and beneath MBT and within the imbricated early Neogene sediments from the northern parts of the frontal belt. Several domal window structures in eastern Himalaya expose low grade pre-Tertiary metasediments occurring beneath the crystalline nappe. The largest Siang window, located close to eastern syntaxis of the Himalaya, is unique and exposes a duplex of Paleogene rocks which have arched, folded and breached MBT. The overlying Himalayan nappe rocks are passively folded. Several nappes in the eastern limb of the dome is greatly attenuated in width and finally overridden by the Trans-Himalayan granitoid nappe. The thrust systems bordering the western limb of the complimentary synform west of the Siang window are obliquely truncated by a N-S trending dextral tear-fault. Further south it merges with the western end of the floor thrust which delineates the southern margin of the Siang half-window. The Siang and other half-windows of eastern Himalaya have many structural similarities and some distinctions. They have been inferred to have evolved in a similar way. The Siang half-window, located close to eastern syntaxis of the Himalaya, was produced by the NE projecting indenter of the Indian continent which acted as an oblique crustal ramp over which the Himalayan and Trans-Himalayan nappes climbed. Convergence of tectonic movements at the eastern syntaxis produced duplex arch in the sub-thrust Paleogene rocks which breached MBT and passively folded overlying Himalayan nappes.

(**Keywords** : Siang window evolution/Indian plant/motion)

Introduction : The Himalaya is mainly made up of thin thrust sheets stacked on one another. The most extensive of these thrust sheets constituting the Higher Himalaya is made up of high grade crystalline rocks, the base of which is identified as the Main Central Thrust (MCT). MCT separates the Higher Himalayan rocks from thrust sheets comprising the Lesser Himalaya to the south. These lower thrust sheets are made up of moderate to low grade Proterozoic metasediments and locally present Late Paleozoic sediments. Over major extent of the eastern Himalaya, the lower most nappe of Late Paleozoic sediments is juxta-posed against and override the Neogene foreland molasse sediments (Siwalik) comprising the Sub-Himalaya. This tectonic contact separating the Tertiary from the overlying pre-Tertiary rocks is generally known as the Main Boundary Thrust (MBT), and same nomenclature is followed here.

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These tectono-stratigraphic thrust packets together with the Sub-Himalayan Tertiary sediments generally occur as linear belts, parallel to the oroclinal trend of the Himalaya. Along the frontal belt MCT and MBT generally have steep northerly dips. Similar occurrences of steep dipping thrust sheets are also reported from the frontal ranges and adjoining foothills from other mountain ranges and are inferred to have resulted mainly from movement and tilting of underlying thrust sheets (Mountjoy,1992). The case for the Himalaya is also similar (Acharyya & Ray, 1982). The original gentler dip of MBT is demonstrated by the presence of an open syn-formal klippe of early Permean and Proteroic rocks of Lesser Himalayan affinity overriding the homoclinal northerly dipping Neogene sediments of the frontal Darjeeling Hills further to the south of the location where MBT generally emerges beneath these pre- Tertiary rocks (Acharyya, 1976).

The Tertiary sequence in the Himalayan foothills consists of both the Paleogene and the Neogene sediments, of which the latter occupies the Sub-Himalayan belt almost continuously. The Paleogene sediments are better exposed in the western Himalaya, as imbricates within the Lesser Himalayan pre-Tertiary rocks, and located beneath the MBT and north of the Neogene sediments (Acharyya & Ray, 1982; Sakai, 1983; Dhital & Kizaki, 1987). Because of relative southward advancement of the allochthonous sheets, the exposed width of the low grade pre-Tertiary metasediments and the Neogene sediments ae very narrow in the eastern Himalaya. The Neogene belt here can be divided into two structural domains which are tectonically juxtaposed. The wider southern domain consists of homoclinal northerly dipping and at times structurally repeated autochthonous Neogene sequence. The homoclinal Neogene sedimens are either tectonically juxtaposed and overridden directly by the pre-Tertiary rocks along MBT, or they are overridden by discontinuous, tectonised early Neogene sedments, which constitute the northern structural domain. The palaeogene sediments are very restricted in occurrence in this part of the mountain range. However, thin thrust slices of marine Eocene rocks are recorded over wide lateral extent, mainly occurring close to and beneath MBT (Fig.1) (Tripathi *et al.* 1979; Acharyya, 1994). In DArjeeling foothills early Miocene open sea-type sediments are also recorded from the tectonised early Neogene unit Kalijhora area (Fig. 1) of (Acharyya *et al.* 1987; Sinha & Srivasava, 1992). Marine nature and wide lateral extent of these thrust slivers mainly occurring beneath MBT and within the tectonised early Neogene sediments imply wide regioal extension of these rocks in subsurface.

The regular arcuate trend of these major thrusts is interrupted at a few locations especially in eastern Himalaya by the presence of domal structures which have affected the crystalline nappe, or even the low-grade Lesser Himalayan nappe (Fig.1). Erosion of the upper level nappes at these sites has carved out half windows which expose subthrust rocks. The possible northern extension of the foreland Tertiery sediments beneath the Lesser Himalayan thrust sheets and in such windows in subsurface have since long been a subject of contention (Acharyya & Ray, 1992; Acharyya, 1994).

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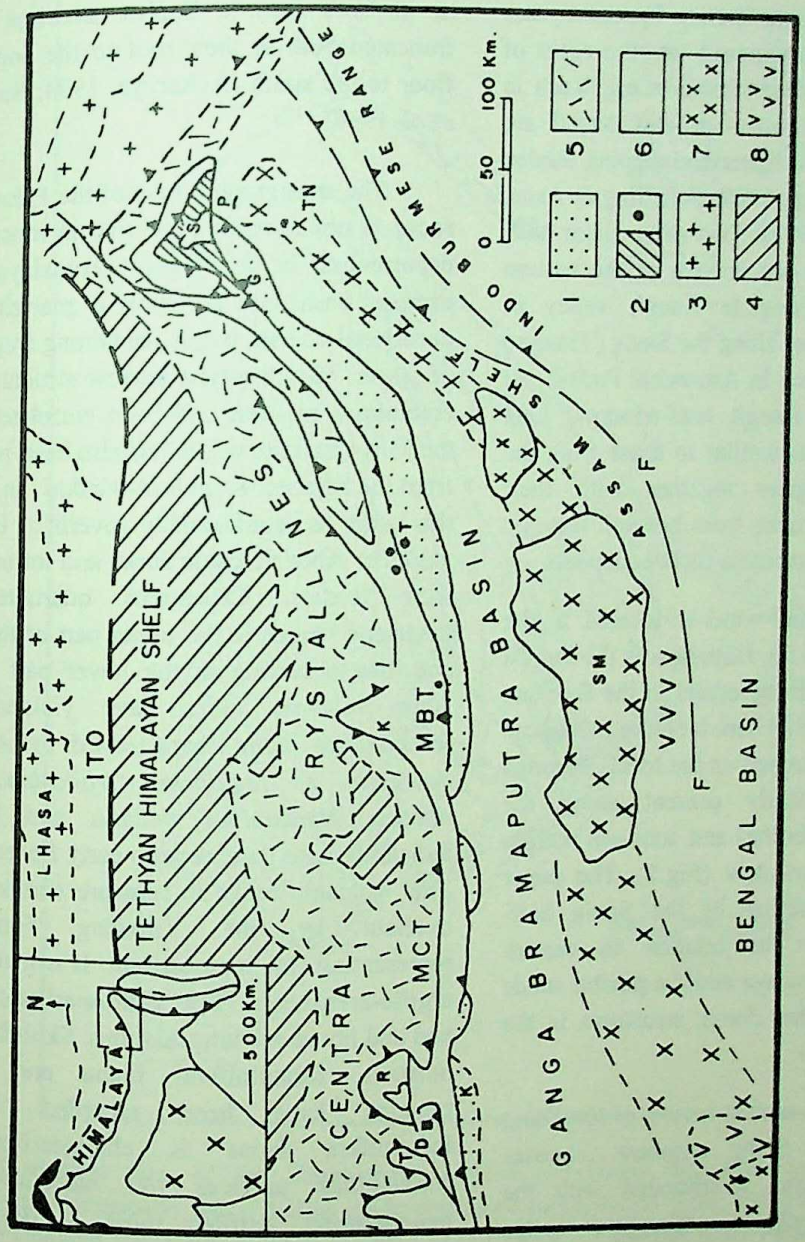

Fig.1– Tectonic of Eastern Himalaya showing location of the Siang and other domal structures. Legend : 1-Neogene sediments, 2-Paleogene sediments/Locations of marine Eocene rocks, 3-Trans- Himalayan granitoids, 4-Tethyan Himalayan sediments, 5-Crystalline rocks of the Himalaya, 6-Lesser Himalayan low grade Proterozoic nappe, 7-precambrian basement rocks of the Indian shield, 8-Cretaceous basalts. Domes : T-Tamar, R-Rangit, K- Kuru, S-Siang, other locations : ITO-Indus Tsangpo Ophiolites, SM-Shillong massif; D-Darjeeling town, G-Garu, K-Kalijhora, P- Pashighat, T-Tipi, Tn-Tenkaghat.

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Such domes in the Himaaya and other mountain belts have traditionally been inferred to result from fold interference. In recent years the subthrust rocks exposed at the cores of two such half-window structures e.g. Kuru in east Bhutan and Tamar in east Nepal are inferred to represent hinterland dipping duplex structures (Ray *et al.* 1989; Schelling & Arita, 1991; Schelling, 1992). Two other major half-window structures are present in the eastern Himalaya, one along te Rangit valley in Sikkim and the other along the Siang (Tsangpo /Brahmaputra) valley in Arunachal Padesh. At the core of the Rangit half-window, Late Paleozoic sediments similar to those from the frontal belt reappear together with their Proterozoic floor rocks from beneath tectonic cover of similar Proterzoic meta-sediments.

The Siang half-window located at the eastern syntaxis of the Himalaya is the largest and differs from all the others in the fact that the sub-thrust material here includes Paleogene rocks which have arched up the MBT. Permian sediments are locally present along the northern (near Dalbuing) and southern margin of th Siang half-window (Fig.2). The paper describes the structure of the Siang half-window, discusses its relation to eastern syntaxis of the Himalaya and the posible mode of evolution of other domal structures in the eastern Himalaya.

Map Pattern and Structure of the Siang Window : The Siang window exposes Paleogene sediments interbanded with the Abor volcanic rocks in a triangular wedge located beneath the arched-up Lesser Himalayan pre-Tertiary rocks to the north. The window is truncated to the south against the Neogene Siwalik sediments, thus it is a half-window. The imbricated Paleogene rocks at its core form a duplex structure being truncated both at their roof to the north and floor to the south (Acharyya, 1994; Sengupta *et al.* 1996).

The stratigraphic base of the Palaeogene rocks is not exposed here like in most other occurrences in the Lesser Himalaya. The exposed basal unit is mainly a quartzite with occasional coarser bands containing fragments of jasper. Skolitho-type burrow structures are common. This unit had been correlated with the Miri Quartzite which has also been mapped from the adjacent Kuru half-window. In Siang, this unit is conformably overlain by the vesicular Abor volcanic rocks and intruded by their feeders. Calcareous quartzite and limestone bands in the upper part of this unit and also occurring in the lower part of the Abor volcanic rocks have yielded rich foraminifera fauna characterised by *Assilina depressa, A. regularia, Orbitosiphon* cf. *tibetica, Nummulites thalicus* and N. sp indicating Late Paleocene to early Eocene age. The volcanic rocks in turn are conformably overlain by the Yinkiong Formation representing the topmost unit. It is mainly an argillo-arenaceous unit with marl,calcareous bed and limestone intercalations. Skolitho-type burrows, foraminiferal fauna and floral remains have been recorded. Larger forminifera fauna is characterised by *Nummulites atacicus, N. maculatus, N. pengaroensis, Assilina spira, A. davies, A subassamica, Orbitolites* cf. *complanata* indicating Mid Eocene age (Acharyya, 1994; Sengupta *et al.* 1996).

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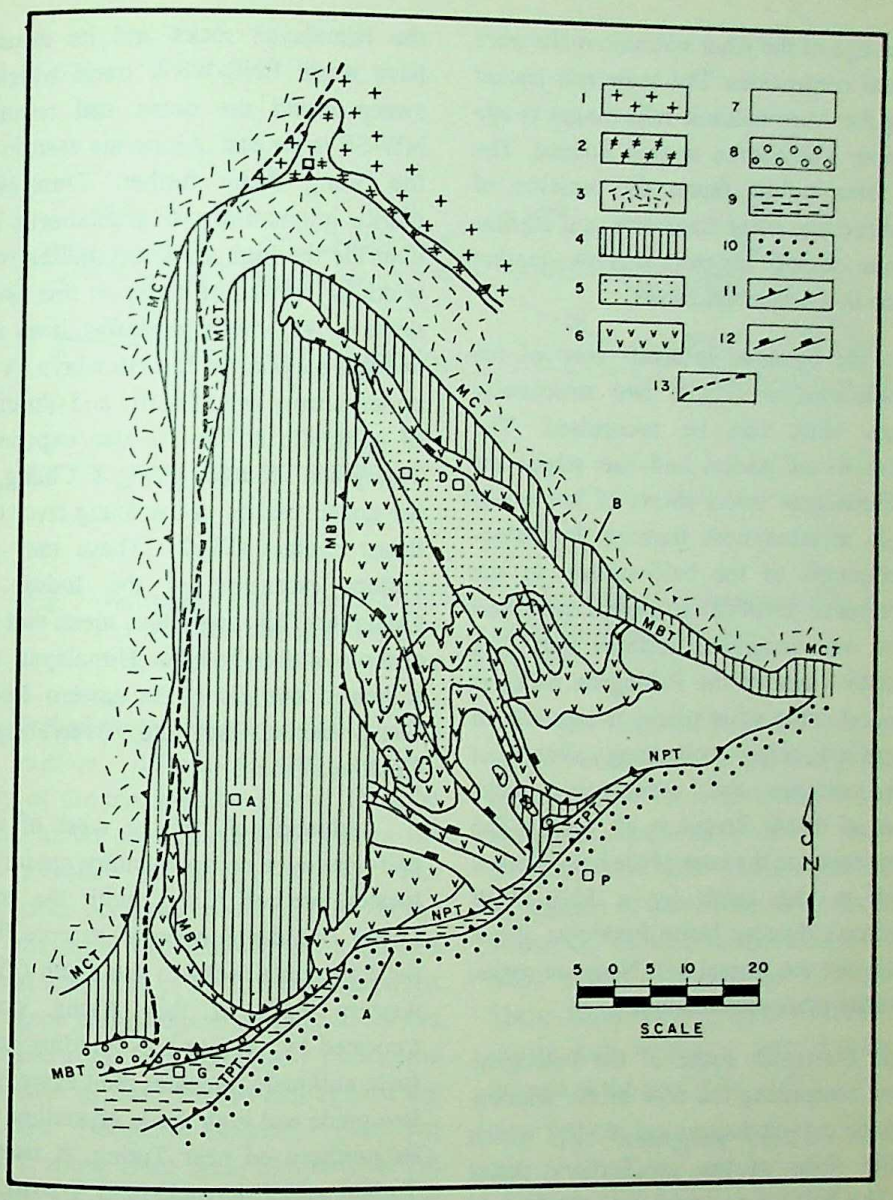

Fig. 2– Geological map of the Siang dome. Legend : 1-Trans- Himalayan granitoid migmatites, 2-Mafic-ultramafic rocks, 3-High grade crystalline rocks, 4-Low grade Proterozoic metasediments, 5-Yinkiong Fm. (Mid Eocene), 6-Abor volcanic rocks, 7-Quartzite (Late Paleocene-early Eocene), 8-Late Paleozoic sediments, 9- Tectonised early Neogene sediments (northern belt), 10-Neogene sediments southern belt, 11-Major Himalayan thrusts, 12-Thrusts within the Paleogene rocks of Siang window, 13-Tuting-Garu Tear fault. Locations : D-Dalbuing, G-Garu, P-Pashighat, T-Tuting, Y- Yinkiong, AB line of section in Fig. 3.

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The age of the Ahor volcanic rocks were so far been contentious. The sediments packet including the Abor volcanic roks ranges in age from Upper Paleocence to mid Eocene. The benthic foraminiferal fauna, the presence of burrow structure, plant fragments and argillo-arenaceous facies suggest shallow marine deposition in a continental shelf.

On the basis of detailed map of the Siang half-window (Fig.2) two structurally discordant units can be recognised. The crystalline thrust packet and the subjeacent Lesser Himalayan thrust sheets of low grade Proterzoic metasediment framing the Paleogene sediments of the half-window to the north, preserve identical structural style and constitute one congruous tectonic unit. The MBT contact against the Paleogene rocks at Dalbuin and some other places is represented by tectonised zones containing slivers of Permian volcanic and sedimentary rocks (Sinha *et al.* 1986; Prasad et al., 1989). The Paleogene rocks in the core of the half-window truncated to the south by a ENE-WSW trending north dipping North Pashighat, thrust (NPT) against the frontal belt Neogene rocks, represent the other tectonic unit.

The triangular shape of the Paleogene sediments comprising the core of the window is due to the curved disposition of MBT which forms the floor of the pre-Tertiary thrust packet. The MBT thus forms a northerly fold closure of the window. Structurally conformable high grade rocks floored by the MCT also define a conformable northerly fold closure.

The Siang half-window is also located very close to the eastern syntaxis of the Himalaya. To the west of this domal structure, the Himalayan rocks and its thrust system have broad ENE-WSW trend which takes a sweep round the dome and trend broadly NW-SE to its east. Along the eastern fringe of the Siang dome further, Trans-Himalayan dioritic migmatites with granodiorite intrusives override the high grade crystalline rocks. The width of crystalline rocks in this limb of the dome is very much narrowed down compared to other sections of the Himalaya. A discontinuous narrow belt of mafic and ultramafic roks of ophiolitic affinity is also exposed around Tuting and Moutuo (Zheng & Chang, 1979) in the upper reaches of the Siang river along this thrust contact (Fig.2). These may represent eastern extension of the Indus- Tsangpo Ophiolite. This would also mean that the entire section of the Tethyan Himalayan rocks are truncated out along the eastern limb of the Siang dome, by the, overriding Trans-Himalayan rocks.

Immediately to the west of the Siang half-window a complimentary open synform is located around Along, with the low grade Lesser Himalayan rocks at its core flanked by the Paleogene rocks to the south (Fig.2). The western limb of this Along synform is truncated by a major N-S trending dextral tear fault. obliquely truncates the Lesser Himalayan low grade and high grade crystalline rocks. At its northern ed near Tuting, it truncates the Tuting ophiolitic rocks and Trans-Himalayan dioritic migmatites, which are juxtaposed against the Himalayan crystalline rocks. At its southern end, it truncates the low grade thrust stack of pre-Tertiary rocks and swerves to join NPT at its western end, near Garu (Fig.2). The tear fault offsets MBT. To its west MBT is aligned along the trace of NPT, whereas to its

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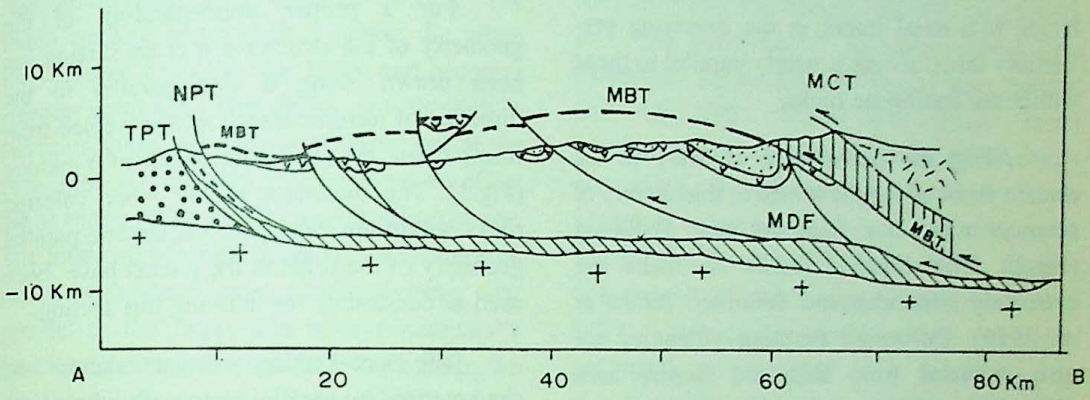

Fig. 3– Structural cross section of Siang half-window along AB. Legend as in Fig. 2. Undifferentiated Paleogene rocks shown by oblique hatching. NPT-North Pashighat Thrust, TPT-Tipi Thrust.

east, it is shifted north, wherefrom MBT with a curved outline delineates the northern boundary of the Siang half-window. Thus the tear fault, at its southern end delineates the western boundary of the half-window. The Permian rocks occurring north of MBT at the western margin of the half-window continues further east and north of NPT, wedged between the Paleogene and Neogene sediments. Slivers of Paleogene rocks are tectonically imbricated near the base of the Permian and against the top of the Neogene seiments from the MBT/NPT zone, Garu area. Similarly at the eastern end of the Siang halfwindow further east, the arched up MBT marking the northern boundary of the Paleogene rocks asymptotically joins with the eastern end of the NPT, and further east MBT has a rectilinear trend located between pre-Tertiary rocks and the Neogene sediments (Fig.2).

The disposition of the Paleogene rocks located at the core of the Siang half-window are controlled by a distinetly different structural style compared to that of the overriding thrust sheets of older rocks. These are dissected by a group of interconnected subsidiary faults. These are oblique in orientation to both the MBT at the roof and the NPT at the floor. These faults usually meet the NPT asymptotically but truncates and dislocates MBT located at the roof (Fig. 2.3).

The Palaeogene rocks are affected by a series of open, upright folds. They show plunge culmination and depression but maintain a consistent NNW-SSE orientation of the axial traces. These folds maintain parallel geometry. The axial traces of these folds maintain strict parallelism with the traces of faults affecting this packet. Change in orientation of the axial traces of these folds

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following the change in strike of the fault traces has produced the complex map pattern of the Palaeogene rocks. The orientation of the major fold axial traces in the overlying pre-Tertiary thrust sheets is nearly parallel to those within the Paleogene rocks.

Along the curve trace of MBT in the eastern flank of the the window, thin slivers of permian rocks are exposed near Dalbuing (Fig.2). The bivalve fossils in them are extremely flattended and deformed (Sinha *et al.* 1986). Deformed Permian volcanics are also recorded from this and nearby area (Prasad *et al.* 1989). Along the same zone the Paleogene basalts are also more intensely deformed than those at the core of the window. North of Yinkiong (Fig.2) the amygdules in the basalts are extremely flattened and stretched forming a strong linear fabric plunging NNE. This linear structure is inferred to lie parallel to the movement direction along MBT.

The concept of balanced cross sections has been introduced to depict the correct geometry of structures (Dahlstrom, 1969). In the area discussed here, no subsurface data derived from bore holes or studies are available and cross section balancing could not be done. However, to the south of the Siang half-window in the alluvial covered Brahmaputra basin, Paleocene to early Eocene marine sediments have been discovered recently at subsurface from Tenkaghat area (Fig.1) occurring near the crestal parts of the buried basement high (Baruah *et al.* 1992). These sediments represent undisturbed counterpart of the Paleogene foreland basin, the continuity of which is observed in the Siang half-window. They have flat dips and consistent bed thickness which have been used to constrain structural cross section (Fig.3).

For a proper understanding of the geometry of the structures a cross section has been drawn along a line parallel to the direction of tectonic transport as revealed from linear fabric decribed from north of Yinkiong (Fig.3). The thickness of the Abor volcanic rocks within the Paleogene packet and parallel geometry of the folds in the packet have been used as constraints for drawing this section.

The pre-Tertiary thrust sheets are characterised by parallel beds, with lithological contacts and planar structures parallel to the thrust planes. They are folded into a pair of N-S trending antiform and synform, which are open folds with rounded hinge (Fig. 2,3). Apparently these folds are confined to the upper thrust sheets and terminate at MBT. The folds affect multiple imbricated thrust sheets consisting of low grade Lesser Himalayan nappe and the crystalline nappe. The character of these folds are comparable to fault-bend folds (Suppe, 1983, 1985), and results due to stepping up of the MBT from a lower to higher detachment horizon along a fronal ramp. As a result bedding in the subthrust Paleogene sequence is truncated at high angle at the ramp. The bedding within the Lesser Himalayana pre-Tertiary nappe dips away from the transport direction, indicating that the upper block has moved over a ramp in the footwall. The arching up of the Paleogene rocks and consequent antiformal fold in the roof nappes are also due to imbricate thrusts and related folds in the sub-thrust block. The folds abve the MBT are discordant with the folds in the subthrust block.

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In contrast, the dislocations in the sub-thrust block broadly have NNW-SSE trend and diverge from a single thrust i.e., NPT and step up through the Paleogene section. The faults usually begin with a gentle dip when they diverge from the sole thrust and becomes steeper upwards. The faults cut through a series of folds and instead of dying out at the core, breach the folds and continue to affect thrust sheets at the roof of the folded sequence. The folds are of uniform shape, asymmetric in nature with steep axial planes dipping near parallel to the faults and always maintain a parallel geometry. The northern back limbs are straight and the southern forelimbs are cut off against the faults. Displacement along all these faults are generally small compared to the overlying MBT and MCT, and in all of them the hanging wall has been upthrown. One antithetic southerly dipping fault diverges from one of these norherly dipping faults, instead of diverging from the sole thrust (Fig.3). The characters of the folds resemble fault propagation folds (Suppe & Medwedeff, 1984, Woodward *et al.* 1989) and the dislocations are comparable in geometry to an imbricate thrust system developed from a system of faults in the sub-thrust block, which are characterised by steeper dips compared to MBT and MCT (Fig. 3). The lithology of the stratigraphic unit involved is suggested to be a major controlling factor governing the formation of fault-propagation folds (Alonso & Teixell, 1992). The dominantly siliciclastic lithology of the Paleogene rocks has favoured the development of such structures in the Siang half-window.

At the southward truncation of the Siang half-window, the imbricate thrust system of the Paleogene rocks is thrust over the tectonised early Neogene sediments across NPT. Two prominent horses of pre-Tertiary Lesser Himalayan rocks are bounded by splays of NPT. The Permian rocks occur near its western end, and Proterozoic carbonates and Late Paleozoic metasediments occur near central part of NPT. These pre-Tertiary rocks represent down faulted klippe of MBT nappe overriding the Paleogene rocks and are juxtaposed against the tectonised early Neogene sediments of the frontal zone. Similar occurrences of pre-Tertiary klippe floored by MBT imbricated within the Neogene sediments are reported from the Darjeeling Sub-Himalaya (Acharyy, 1976, 1994). The relation is also very similar to the Rocky valley anticline and Rocky valley thrust (Fischer & Woodward, 1992). Thrust slivers of marine Eocene sediments and volcanics are also exposed elsewhere further south at the base of the hanging-walls of imbricate thrusts within the tectonised arly Neogene unit (Acharyya, 1994). The entire tectonised sequence of early Neogene and older rocks rest against the northerly dipping homoclinal autochthonous Neogene sediments along the Tipi thrust (Fig. 2.3).

Comparison with other Domal Structure in Eastern Himalaya : Among the domal structures in the Himalaya extending between the Siang valley in the east to eastern Nepal in the west (Fig. 1), the Siang dome has certain significant distinctions. The common features in all these half-windows are their uparched and folded northern tectonic margin and mainly rectilinear southern margin. All the domes except the Siang are mainly defined by the up-arched northerly dipping MCT which asymmetrically bound them on three sides. At

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the cores of these windows low grade Proterozoic meta-sediments, wedge of basement granite-gneiss with or without Late Paleozoic sediments are exposed which occur beneath the high grade crystalline rocks. In contrast, the Siang half-window by the uparched MBT and Paleogene rocks are exposed at the core occurring beneath the pre-Tertiary meta- sediments.

The adjacently located Tamar and Rangit half-windows are closed similar. The Tamar Khola Thrust (TKT) delineating the southern margin of the Tamar half-window appears to join with the Rangit-Raman Thrust (RRT) system further east which delimits the southern boundary of the Rangit half-window (Fig. 1). In the Kuru half-window the southerly located Shumar thrust (Ray *et al.* 1989) can be compared to TKT and RRT. In the Siang half-window the comparable structural element is NPT.

In the non-balanced structural cross-section through the Tamar half-window, Schelling and Arita (1991) and Schelling (1992), inferred that the window rocks occur as hinterland dipping arched-up duplex (Fig. 4). The MCT, TKT, MBT, and the thrusts within the Sub-Himalayan Neogene belt and the Main Frontal Thrust (MFT) at its frontal termination are all linked to a single Main Detachment Fault (MDF). MDF is located at the lower crustal level in northern and internal parts of the Himalaya, where from MCT has branched and ramped up. In the process of advancing towards the frontal zone, the Main detachment fault progressively climbed up to upper structural/stratigraphic levels. The Tamar Khola Thrust branched up from the Main Detachment Fault located beneath the Tamar window and within the granitoid basement rocks of the Proterozoic metasediments. It appears to have climbed a north dipping ramp and a thrust-fault, and then surfaced as a steep dipping thrust (Fig. 4). As a result the hinterland dipping horse comprising the low grade Proterozoic rocks and its granitoid basement rocks are arched up as a fault-bend antiform which passively folded overlying MCT. Schelling and Arita (1991) and Schelling (1992) based their structural cross section assuming direct stratigraphic linkage of the allochthonous Lesser Himalayan Proterozoic metasediments with the basement rocks of the foreland basin which is not justified. They further assumed that the Neogene foreland basin terminated against the steeply dipping MBT. Thus their models preclude the possibility of extension of the Tertiary foreland sediments extending beneath MBT, and consequent structural influence of these rocks on the overlying pre-Tertiary nappes.

In the Rangit half-window the southern boundary is delimited by a broadly east-west trending north dipping Rangit-Raman Thrust system. These thrusts truncate the southern boundary of the Late Paleozoic sediments of the window and bring them to juxtaposition against the Peoterzoic low grade rocks. These also truncate the older thrust continuing from the northern end of the window and delineating the tectonic base of the allochthonous Proterozoic metasediments overriding the Late Paleozoic sediments of the window (Fig. 4). Further south within Daling-tupe low grade Proterozoic metasediments and along the southern thrust of the RRT system highly deformed Late Paleozoic rocks have been

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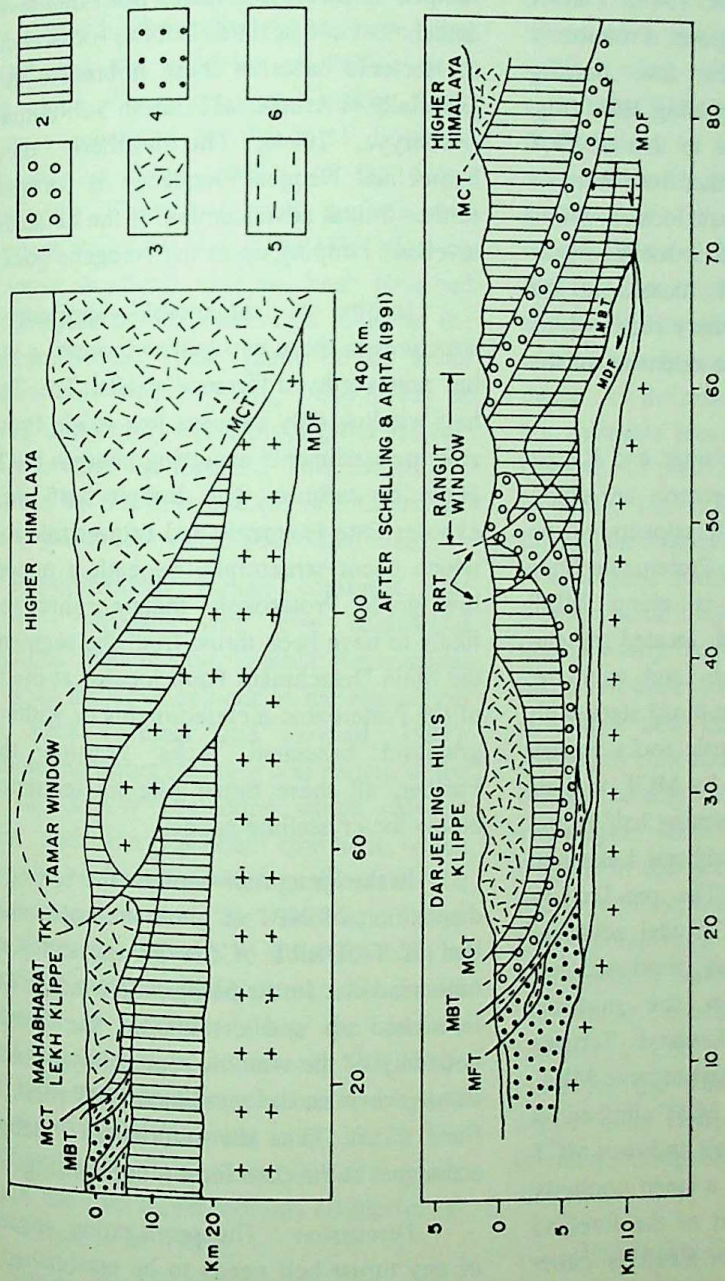

Fig. 4.–Structural cross section of Tamar and Rangit half- windows. Legend : 1-Late Paleozoic Sediments, 2-Low grade Proterozoic metasediments, 3-High grade crystaline nappe of the Himalaya, 4-Crystalline basement and granitoid rocks of the Himalayan forland, 5-Paleogene sediments, 6-Tectonised early Neogene sediments, 7-Autochthonous Neogene sediments. (5-6-7 Corresponds to the Himalayan foreland basin). Tamar window structural section after Schelling and Arita (1991). The section has been drawn assuming allochthanous Proterozoic rock of the Lesser Himalaya to directly underlie the autochthonous Neogene, and the Neogene basin to terminate against the steeply dipping MBT. The structural cross section of Rangit Valley window on the other hand drawn assuming the northern extension of the foreland Tertiary basin nearly up to the window zone.

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mapped occurring within a narrow zone of lithostratigraphically distinct Reang-type Proterozoic rocks (Acharyya, 1989). Further south in turn, the low grade Proterozoic metasediments underlie the low dipping crystalline rocks of the Darjeeling Hills (Fig. 4). The RRT system similar to that of TKT appear to climb up a ramp either from that part of the Main Detachment Fault located within the low grade Proterozoic floor rocks or may even ramp up from MBT located at the tectonic base of the pre-Tertiary rocks which have overridden the northern extension of the Tertiary sediments (Fig. 4).

Further south of the Tamar and Rangit half-windows, tectonic movements are along the Main Detachment Fault appears to be located within the low grade Proterozoic floor rocks or the movement is along MBT following a thrust-flat and located at the tectonic base of pre-Tertiary and over the sub-thrust Tertiary rocks. The thrust stack with exposed low grade Proterozoic rocks carries the crystalline nappe floored by MCT on their back. This has resulted in forming half klippe of crystalline rocks at Mahabharat Lekh and Darjeeling Hills (Fig. 4). The pre-Tertiary thrust stack at this stage of frontal advancement or even earlier as already mentioned, has encroached and overridden the northern sub-thrust extensions of foreland Tertiary sediments. Thus the floor thrust became MBT. After following a thrust-flat, MBT climbed up a ramp close to the frontal belt and thus MCT and MBT are exposed with a steep northerly dip. Within the exposed part of the foreland basin, the Main Detachment Fault is either located within the early Neogene sequence (Lower Siwalik) or within the marine Eocene sediments (Fig. 4). The tectonised of early Neogene frontal belt sediments represent ramped up thrust imbricates from this level of detachment and at times Eocene rocks occur at the tectonic bases of these imbracate thrusts especially in Arunachal Pradesh Sub-Himalaya (Acharyya, 1994). The northerly dipping homoclinal Neogene sequence is formed by further frontal advancement of the detachment level and ramping up of the Neogene pack.

Inspite of remarkable similarity of structures in these two half- windows, a minor but noteworthy difference exists. The Tamar half-window only exposes low grade Proterozoic metasediments occurring beneath the high grade crystallines. The Rangit half-window exposes Late Paleozoic and Proterozoic rocks, which occur structurally beneath a nappe of low grade Proterozoic metamorphic rocks, likely to have been thrust from the segment of the Main Detachment Fault located at the base of the Proterozoic metasediments or within the granitoid basement rocks flooring them. Further, all these thrust pile lie tectonically below the crystalline nappe.

In the Siang half-window the setting and disposition of NPT is closely comparable to that of TKT/RRT of the Tamar and Rangit half-windows. In the Siang half-window MBT is arched up and demarkates the northern boundary of the window representing the roof thrust, whereas, the rectilinear NPT marks the floor thrust. Thus the imbricated Paleogene sediments at the core form a duplex (Fig. 3).

Discussion : The propagation sequence of any thrust belt needs to be established for understanding the evolution of a fold-thrust sequence. In the structural unit consisting of

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the crystalline nappe and the Lesser Himalayan low grade pre-Tertiary metasedimentary nappe, thrust and thrust sequence propagated from north to south, the lower thrust sheet being younger and the overlying crystalline sheet being older. This upper pre-Tertiary thrust packet is separated by the MBT from the paleogene sub-thrust packet of the Siang half-window. These two thrust packets have discordant structural style. The MBT flooring this upper structural unit has been breached and disrupted by the system of faults in the sub-thrust block. These faults in the lower structural unit are thus younger and it may be inferred that deformation propagated systematically towards the foreland. This inference is supported by the development of the foreland basin on the Indian shield (Burbank, 1983).

Pre-collisional Indian continent was effective Y-shaped with two continental projections, which have exerted fundamental control on the development of the Himalayan thrust stack (Treloar and Coward, 1991). Collision and thrust stacking was earliest at the point of its NW projection which collided earliest with the Eurasian continent which ultimately became the western syntaxis. The thrust propagation along the two oblique slopes of this diamond shaped NW indenter would be the same as along an oblique ramp. Movement on thrusts in Pakistan along the western leading edge was directed towards SSE, while in the Indian region along the eastern edge, it was towards SSW (Coward *et al.* 1987). The NW Himalaya is thus a zone of convergence between the two thrust systems (Butler *et al.* 1989; Treloar *et al.* 1992).

Since the initial collision during early-middle Eocene at the NW projection, Indian plate has rotated anticlockwise with increased amounts of subduction to the east (Dewey *et al.* 1989). The north-easterly protuberance in the Indian continent acted as the indenter when collision occurred in the eastern end of the Himalaya. This has resulted in the development of the eastern syntaxis having some similarity in character to the western syntaxis. For propagating thrust within the Indian plate the NE indenter with a northerly sense of movement acted as an oblique ramp and resulted in development of ramp anticline in the crystaline and in the pre-Tertiary MBT nappe. All the major Himalayan thrust systems are traceable around this antiformal structure but some of these have been greatly attenuated in width. The Trans-Himalayan granitoid and crystalline nappes are pushed forward to the frontal zone further SE of the Siang half-window and they virtually lie against the north-easterly projected Indian shield basement. All the external tectonic features of the Himalaya and those of the Indo-Burmese Range are concealed beneath and truncated by these frontally advanced NW-SE trending Himalayan and Trans-Himalayan nappes (Fig.1). In this sector the NE indenter of the Indian continent as well as, the continental block comprising the Indo-Burmese mobile belt which is sutured to the NE projection of the Indian continent since late Miocene (Acharyya, 1996), together acted as a frontal ramp for the frontally advanced crystalline nappe and Trans-Himalayan nappe, being oriented orthogonal to the tectonic transport direction.

The Tuting-Garu dextral tear fault along the western margin of the Along synform has many similarities with the faults affecting the

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Paleogene sub-thrust rocks of the Siang half-window. It branches from the NPT floor thrust, has the same sense of tectonic movement, and not only breaches MBT roof-thrust but also MCT and the crystalline nappe. Thus temporally the tear-fault movement was younger to MBT as those sub-thrusts of the Siang half-window. Tear faults are also reported from the western syntaxis of the Himalaya and are produced because of change of movement vector of thrusts at the two sides of the NW indenting front to the Indian continent (Coward *et al.* 1987; Treloar *et al.* 1992). The Tuting-Garu dextral tear fault cannot be accounted by the impingement of the NE indenter which would have resulted sinistral fault. The dextral tear instead is inferred to have resulted because of movement within the sub-trust Paleogene rocks as those within the Siang half-window. But it has breached through the overlying Himalayan nappes, and thus might have accommodated late stage differential movements of nappes located on its either side. Thus the process controlling the development of tear faults at the western and eastern syntaxes are district from each other.

The tectonic movements on the Himalayan thrusts along the eastern edge of the NE indenter was towards SSW, which is confirmed by the kinematic indicators present in the rocks here. In contrast, movement on thrusts along the western edge of this indenter is towards SSE, making this a zone of convergence. Major thrust sheets were emplaced over the Paleogene foreland rocks located within this zone of convergence and close to the eastern syntaxis of the Himalaya. The required crustal shortening was accommodated in the subthrust block by younger reverse faults and fault- propagation folds. All these provided unique setting for the Siang dome which are responsible for its typical features.

The sub-thrust structures as well as, the Tuting-Garu tear fault have affected the roof thrust packet which played a passive role and at place was subjected to extension and faulting. The former are likely to have modified the antiformal structures thereby their amplitude-wavelength ratios. The structure in the overlying unit may therefore be designated as a hybrid antiform. The greater structural relief observed in case of the Siang half-window is possibly due to the hybrid nature of the structure.

The close structural similarity between Tamar, Rangit and Siang half-Windows indicate some genetic connection in their development. Their isolated nature of occurrence are unlikely to have been caused by type-I interference of folds. Similar domes are common along external fringes of large thrust sheets and are also occupied by duplexes. These are interpreted to have been formed as a response to the implement of the crystalline thrust sheets and subthrust architecture (Elliot and Johnson, 1980; Mitra 1986; Hatcher, 1991). In the Siang dome, the high grade crystalline and the low grade metasedimentary sheets are arched up because of the duplex architecture of the sub-thrust Paleogene rocks. In the Kuru dome the uparched geometry of the crystalline sheet is associated with duplex structure in the Lesser Himalayan low grade metamorphic rocks (Ray *et al.* 1989). Horses of deformed granitiod rocks are exposed in this

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and in Tamar half- window. In the Kuru dome these have yielded a Precambrian age and possibly represent basement rocks (Sinha Roy and Sengupta, 1986). Thus these duplexes must have been formed when the main thrust motion was over the Lesser Himalayan Proterozoic rocks including their continental basement. Subsequently when the thrust encroached over the Tertiary foreland basin, the thrust motion got transferred to MBT and the earlier formed duplexes would be carried passively on top of MBT. The presence of marine Eocene and early Miocene open sea type marine fauna close to MBT over wide strike length in the frontal belt from the eastern Himalaya (Acharyya *et al.* 1987; Acharyya, 1994; Sinha and Srivastava, 1992), as well as, the presence of marine Paleogene sediments imbricated within the Lesser Himalayan metasediments in central Nepal Himalaya (Sakai, 1983; Dhital and Kizaki, 1987) indicate the encroachment and involvement of the northern parts of the Tertiary foreland basin during the movement along MBT. The map pattern at the present level, however, does not reveal uparching of MBT and the sub-thrust Tertiary sediments in the other windows as against that in Siang.

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A seismic hazard and risk scenario for Himalaya and Ganga plains due to a future great earthquake

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Abstract : Strong ground motion time histories are synthesized using the composite source model at a few sites for a prototype gap filling M_w 8.5 great earthquake in the western side of the central seismic gap in Himalaya which extends from the Bhagirathi valley in the west to the Kali valley in the east. The peak ground accelerations attain values around 1 g in the regions overlying the fault plane. In the Ganga plains the values vary from 0.32 g to 0.7 g depending on the distance from the fault plane. The damage potential of such an earthquake is extreme. The possibilities of its compounding due to failure civil works like high dams exist. The loss of human lives could be over several hundred thousand and economic loss of hundreds of billion Rupees. A further scenario was developed for an extentional type of earthquake (M_w 6) in the Ganga foredeep at a short epicentral distance. This showed that peak ground acceleration of about 0.32 g can be produced exposing the effected regions to considerable hazard.

(**Key words** : seismic hazard/Himalaya and Ganga plain)

Introduction : The arcuate mountains of Himalaya harbor one of the more active seismic belts of the earth. This belt has experienced four great earthquakes in the past 100 years claiming several thousand lives (Oldham, 1889; Middlemiss, 1910; Dunn, 1939; Rao, 1953) (Fig. 1). Most of the losses came in the 1905 Kangra and the 1934 Bihar earthquakes which occurred in populated centers. The 1987 and the 1950 Assam earthquakes were in areas of sparse population. Due to population explosion the recent decades the region of Lesser Himalaya has become quite densely populated. In order to tap the enormous hydro-electricity and water resources of Himalaya a number of high storage dams and associated power plants have come up, while many more are planned (Fig.2). In the adjoining Ganga plains on the southern side the growth of population and industry has been even more phenomenal.

Thus, the risk due to seismicity has multiplied manifolds now. For example Arya (1990) has estimated that a repeat of the 1905 great earquake now could claim well over 350,000 lives.

The foremost societal responsibility of seismologists is to provide accurate assessment of earthquake hazard which may serve as an appropriate basis for seismic risk mitigation. As the earthquake processes and their effects have aspects of randomness the hazard assessments often are made in terms of probabilistic models of earthquake occurrence. However, the occurrences of great earthquakes in a seismic zone such as the Himalaya needs

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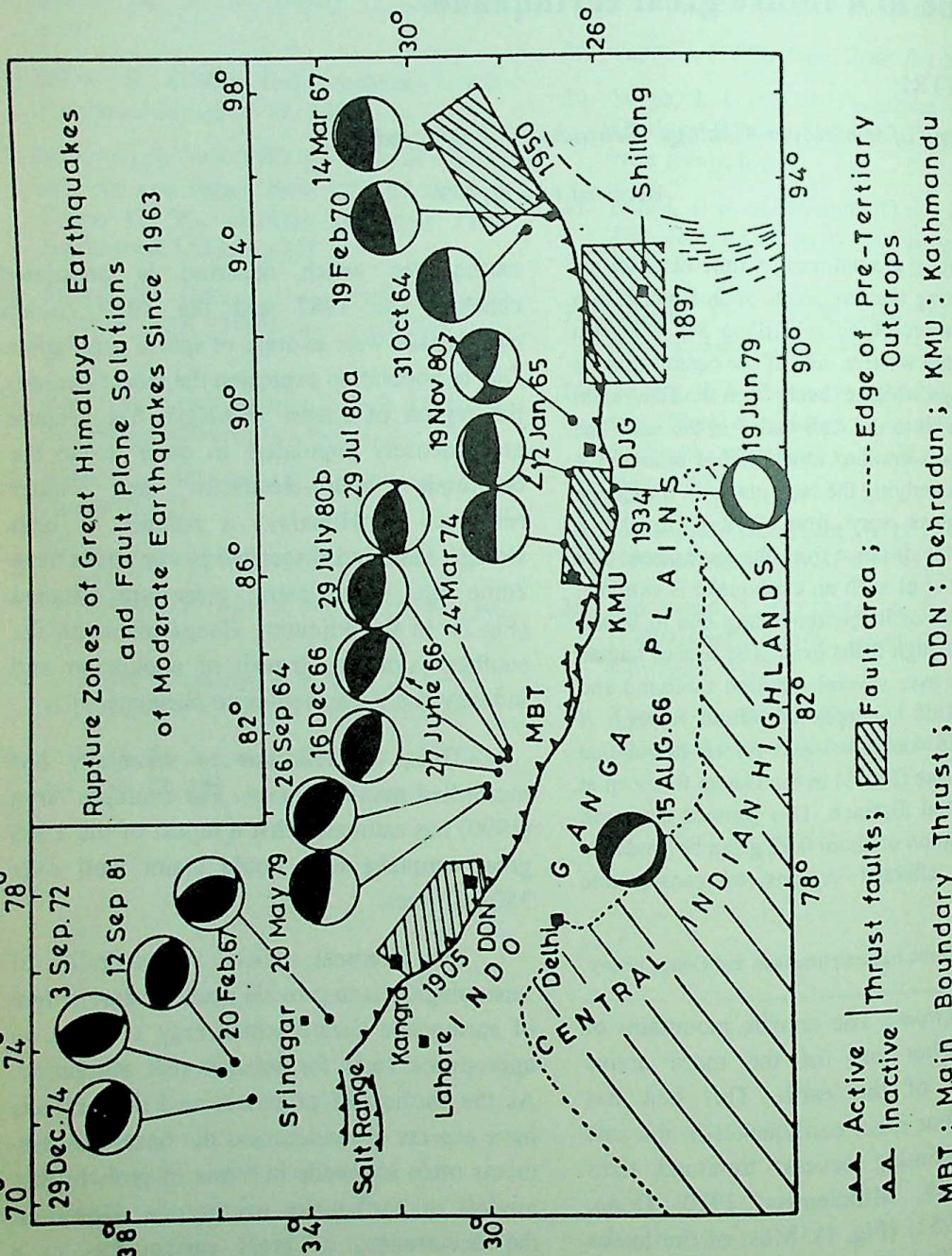

Fig. 1–The rupture zones of great Himalaya earthqukes and the fault plane solutions of medium sized earthquakes (adopted from Molnar, 1990)

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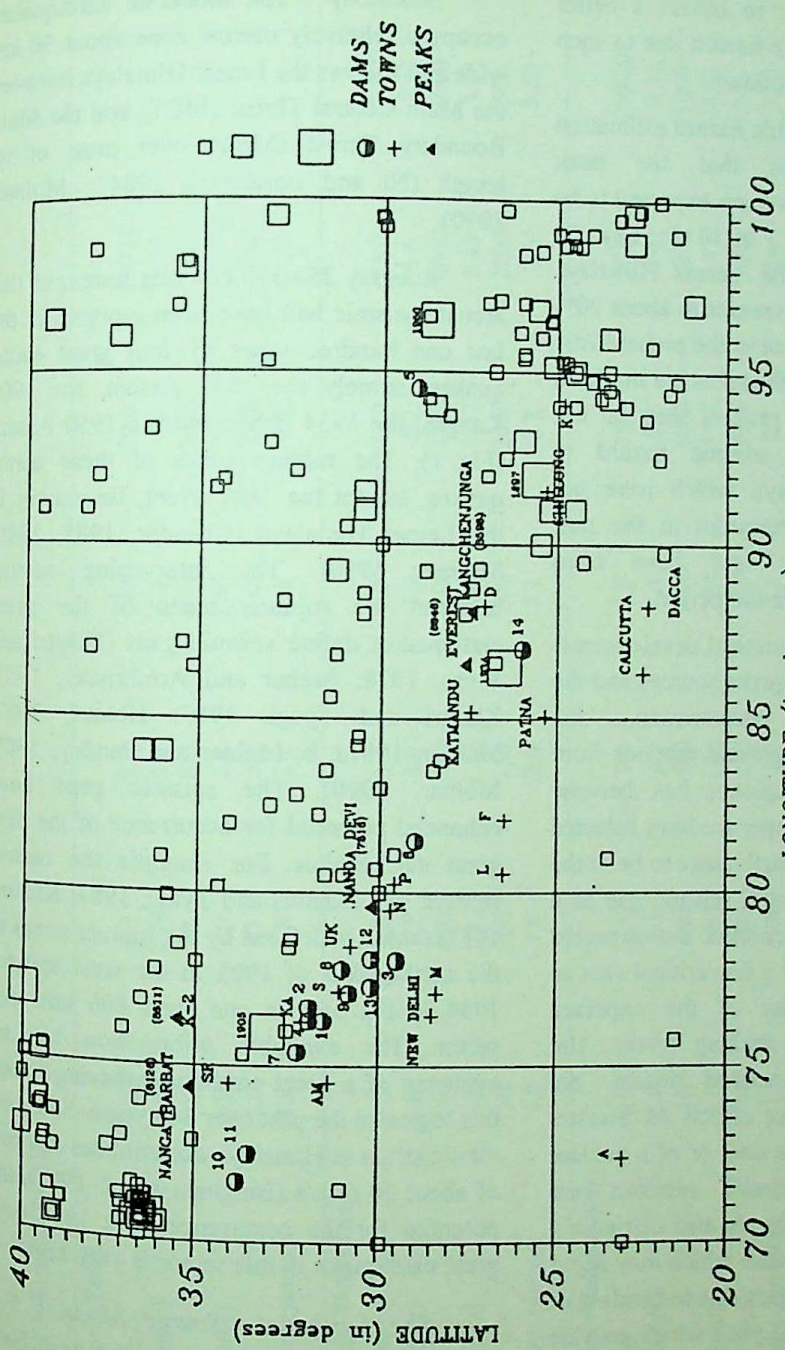

Towns : S-Simla, N-Nainital, P-Pithoragarh, D-Darjeeling, K-Kohima AM-Amritsar, L-Lucknow, F-Faizabad, SR-Srinagar, A- Ahmadabad, M-Moradabad
Dams : 1-Bhakra, 2-Pandoh, 3-Kalagarh, 4-Pong, 5-Dihang, 6- Karnali, 7-Tein 8-Kothar, 9-Kishau, 10-Tarbela, 11-Mangla, 12- Tehri, 13-Lakhwar, 14-Koshi

Fig. 2–The location of larger earthquakes and the river valley projects in Himalaya.

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special analysis in order to obtain a better appraisal of the earthquake hazard due to such events in specific time windows.

A probabilistic seismic hazard estimation for the region shows that the peak accelerations of over 70% g are expected to be exceeded at the rate of 1 in 10 in any 50 year time interval in the Lesser Himalaya (Khatri *et al.* 1984). It decreases to about 20% g in the Ganga plains. Since in the probabilistic hazard estimation the earthquakes are modeled as a stationary Poisson process they do not reflect the heightened seismic hazard in seismic gaps in Himalaya which have not experienced a great earthquake in the past several hundred years and have been elsatically storing strain in the period.

With the recent theoretical developments in the modelling of earthquake sources and the wave propagation phenomenon the calculations of expected ground motions from anticipated future earthquakes has become feasible. In the present paper we have selected the site of a future great earthquake to lie in the western sector of the central seismic gap as a prototype and have calculated the expected strong ground motions at a few critical sites to illustrate the high order of the expected severity of the ground shaking forces. The potential of the associated losses are visualized. The multiplier effects on disaster from possible failure of a dam or of a nuclear power due to earthquake motions are discussed. The simulations are also carried out for an extentional earthquake which may occur in the Ganga foredeep region due to bending of the under thrusting Indian plate which provide a basis for estimating the seismic hazard there due to such earthquakes.

Seismicity : The moderate earthquakes occupy a relatively narrow zone about 50 km wide and follows the Lesser Himalaya between the Main Central Thrust (MCT) and the Main Boundary Thrust (MBT) over most of its length (Ni and Barazangi, 1984 : Molnar, 1990).

Roughly 250-300 km long sectors of this arcuate seismic belt have been ruptured in the last one hundred years by four great earthquakes, namely the 1897 Assam, the 1905 Kangra, the 1934 Bihar and the 1950 Assam (Fig. 1). The rupture zones of these earthquakes, except the 1897 event, lie mainly in the Lesser Himalaya (Chander, 1988, 1989; Molnar, 1990). The intervening sectors between the rupture zones of the great earthquakes define seismic gaps (Khattri and Wyss, 1978; Seeber and Armbruster, 1981; Khattri and Tyagi, 1983; Khattri, 1987; Molnar, 1987a, b; Molnar and Pandey, 1989; Molnar, 1990). The seismic gaps have enhanced potential for occurrence of the next great earthquakes. For example the central seismic gap (Khattri and Tyagi, 1983; Khattri, 1987) which is defined by the rupture zones of the earthquakes of 1905 in the west and the 1934 in the east is one such 800 km long sector. The available information has no evidence of a great earthquake having struck this region in the past over 300 years. Since the elastic strain in Himalaya accumulates at a rate of about 20 mm/a (Bingham *et. al.* 1997), the potential for the occurrence of a 1934 type great earthquake in this sector is very high.

The Earthquake Source Model : For calculating ground motions in the near field (distances related to fault dimension) of an

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Table 1–Velocity Models

Station : **Tehri**							
H (km)	0.05	0.5	2.0	14.0	30.0	1000.0	
Vp (km/s)	0.90	1.75	4.0	5.2	6.0	8.33	
Qp	10	30	100	4000	4000	1000	
Vs (km/s)	0.50	1.0	2.8	2.97	3.43	4.83	
Qs	5.0	15	50	2000	2000	500	
Density (gm/cc)	1.8	1.8	2.4	2.6	2.9	3.33	
Station : **Dehradun**							
H (km)	0.05	1.0	3.0	2.5	15.0	18.0	1000.0
Vp (km/s)	1.80	2.3	3.0	4.4	5.2	6.6	8.33
Qp	100	400	500	1000	4000	4000	1000
Vs (km/s)	1.04	1.33	1.73	2.54	2.97	3.43	4.83
Qs	50	200	250	500	2000	2000	500
Density (gm/cc)	1.8	1.8	2.0	2.1	2.2	2.6	3.30
Station : **Saharanpur**							
H (km)	0.05	1.0	3.0	2.5	15.0	18.0	1000.0
Vp (km/s)	1.80	2.3	3.0	4.4	5.2	6.6	8.33
Qp	100	400	500	1000	4000	4000	1000
Vs (km/s)	1.04	1.33	1.73	2.54	2.97	3.43	4.83
Qs	50	200	250	500	2000	2000	500
Density (gm/cc)	1.8	1.8	2.0	2.1	2.2	2.6	3.30
Station : **Narora**							
H (km)	0.10	1.0	4.0	6.0	10.0	2.0.0	1000.0
Vp (km/s)	0.9	2.3	4.06	5.31	6.57	6.89	7.33
Qp	30	400	1000	4000	4000	4000	1000
Vs(km/s)	0.50	1.33	2.34	3.06	3.80	4.98	4.52
Qs	15	200	500	2000	2000	2000	500
Density (gm/cc)	1.8	1.8	2.66	2.72	3.0	3.08	3.29

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earthquake which have a character of randomness the finite extent of the fault plane and the nature of rupture which is highly irregular has to be taken into account. In order to model these aspects the faulting in the main event is represented as a superposition of smaller sub-faults, which are circular in shape and their radiuses and centers are distributed randomly over the earthquake fault plane. Their areas may overlap. However, the sub-events stay with in the fault plane of the main event. The total seismic moment of the sub-faults is equal to the seismic moment of the main earthquake. The stress drop in the sub-faults is assumed to be constant. The earthquake rupture is allowed to commence from the hypocenter and as the rupture front expands and touches the center of a sub-event (fault) it radiates a Brune pulse (Brune, 1970). This models the rupture propagation directivity effects. The radiation pattern is governed by the dislocation model (Zeng *et al.* 1993; Khattri *et al.* 1994). The source time function corresponding to the radiations from all the sub-events is obtained by the superposition of the Brune pulses for all the sub-events. The pulses from sub-events are appropriately shifted for the time delays with reference to the *S* phase travel time for the pulse from the hypocenter and the travel times of the *S* phase from the sub-events to the observation site as well as for the rupture propagation delays before summing. Thus the earthquake model parameters consist of the dimension, fault plane solution, the seismic moment, sub-event stress drop, rupture velocity and rupture start-point.

The Green's functions are calculated using the velocity-density-Q model for the region and the fault plane solution using wave number integration method (Luco and Apsel, 1983). This is a time consuming calculation and the sun-events are very large in number. Therefore, to economize on computation time, the fault plane is divided into a suitable number of grids and the Green's functions are calculated for these grids. The source time functions are also obtained for the corresponding grids. These two are convolved for each grid and summed to provide the accelerogram at the site (Khattri *et al.* 1994). The method has been found to be successful in modeling the observed strong ground motions from earthquakes in different seismo-tectonic environments as well as a wide range of magnitudes (Zog *et al.* 1993; Khattri *et al.* 1994; Yu *et al.* 1995; Sri Ram and Khattri, 1997). Thus we may use it for prognostication of strong ground motions from probable future earthquakes.

Results and Prognostications : The fault planes of the moderate earthquakes dip northward at low angles (Fig. 1). The slip in the great earthquakes takes place on a detachment which dips at a low angle to the north (Seeber and Armbruster, 1981; Molnar, 1990; Chander, 1988, 1989). The moderate earthquakes occur at the northern edge of this detachment. Accordingly the location of the surface projection of the fault plane of the prototype earthquake shown in Fig. 3 is adopted for ground motion simulations.

Taking into consideration the magnitudes of previous great earthquakes in Himalaya a magnitude of M_w 8.5 having a corresponding seismic moment of M_0 6×10^{28} dyne cm is selected for the probable

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Table 2-Values of Peak Ground Motion Parameters

Station/E		stress drop	E-W				N-S				Z			
			pga	sd	pgv	sd	pga	sd	pgv	sd	pga	sd	pgv	sd
MAGNITUDE M_w 8.5														
TEH	A	100	542	83	88	18	778	323	117	16	843	322	135	38
TEH	B	100	494	98	74	13	970	327	151	36	908	247	146	30
TEH	B	70	431	64	75	15	685	89	136	6	756	96	133	28
DDN	B	100	565	92	187	22	706	90	213	29	545	139	149	17
DDN	B	70	485	102	188	10	629	15	231	33	432	48	135	22
SAH	B	100	442	43	175	40	543	133	127	21	382	82	128	33
SAH	B	70	369	32	192	29	446	128	128	23	295	38	128	25
NAR	B	100	255	34	73	20	478	102	150	28	265	54	109	73
NAR	B	70	184	45	56	13	324	14	109	16	232	32	88	15
MAGNITUDE M_w 6														
NAR		70	73	13	7	2	373	63	32	7	41	12	3	1

Note : The accelerations are in cm/sq s and velocities are in cm/s

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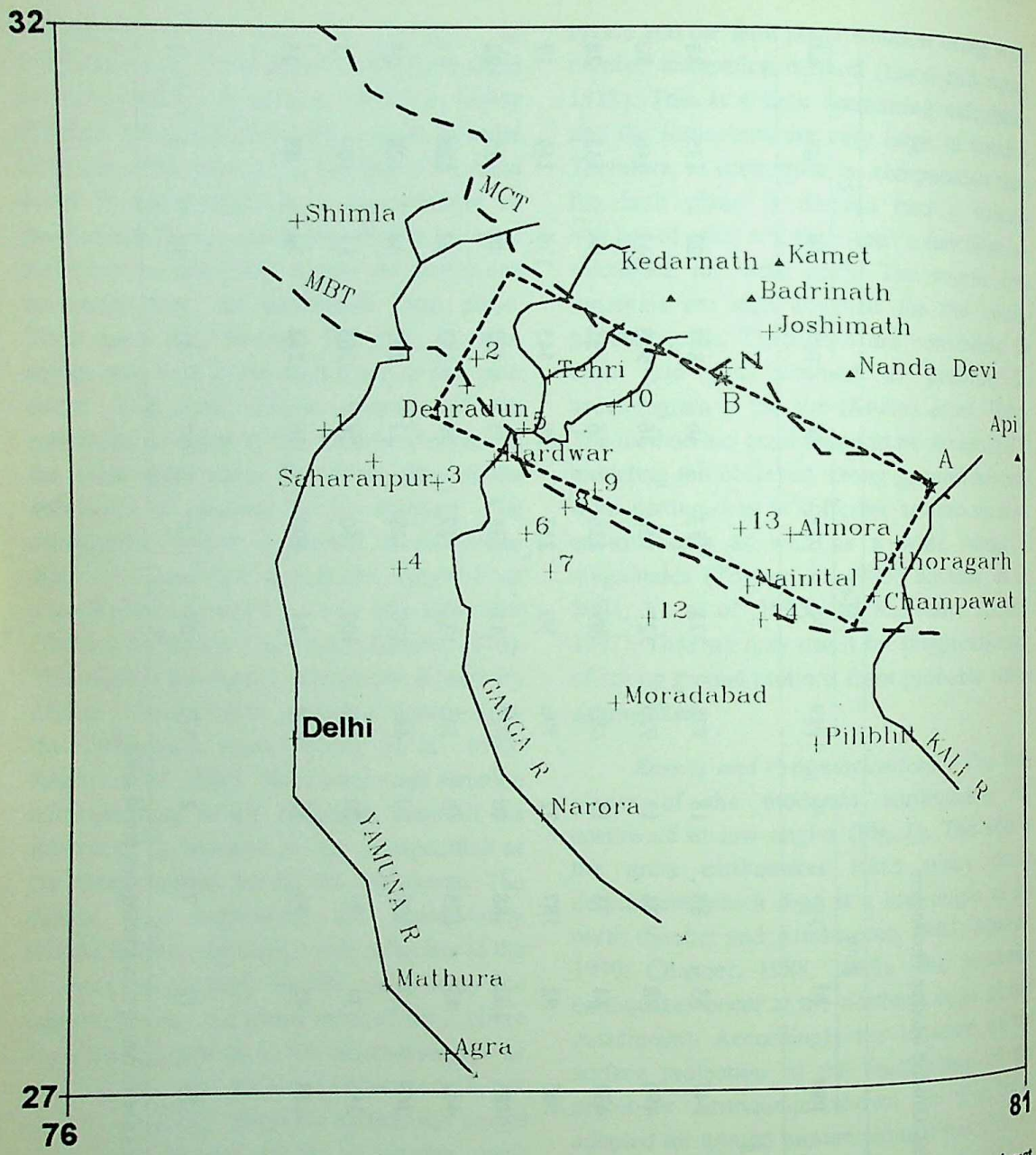

Fig 3–The fault model for the M_w 8.5 earthquake. A and B are epicenters. MBT : main boundary thrust. MCT: Main central thrust-1 : Yamunanagar, 2 : Mussorie, 3 : Roorkee. 4 : Mufaffarnagar, 5 : Rishikesh, 6 : Najibabad, 7 : Nagina, 8 : Kotdwar, 9 : Lansdown. 10 : Srinagar, 11 : Chamoli, 12 : Kashipur, 13 : Ranikhet, 14 : Haldwani.

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hypothetical event. The size of the fault plane is 240 by 80 km which lies approximately between the MCT in the north and MBT in the south. The dip of the fault plane is 60 to the north east with its deeper edge (northern edge) at a depth of 18 km. The strike of the fault is 314° and slip is of thrust type (rake = 90°). Simulations of strong ground motions were done for Tehri which is the site for the construction of a 265 m high dam, the towns of Dehradun, Saharanpur and Narora, where a nuclear power plant is operating. The sites are shown in Figure 6. Of these the first two sites are lying above the fault plane while the last one is about 200 km away. The velocity-Q models used for each site were adopted on the basis of available seismological information (Khattri, 1992; Chun, 1986; Choudhary, 1966), simulations of strong ground motions of the 1991 Uttarkashi earthquake (Khattri *et al.* 1994; Yu *et al.* 1995) and geophysical exploration for oil in Ganga plains. These are shown in Table 1.

The Himalaya is the site of continental collision and very high elevation. A continental collision zone will have higher coupling between the colliding plates resulting in high levels of tectonic stresses (Cloeting and Wortel, 1986; Singh, 1981). Static stress drops of about 60 bars have been estimated for large earthquakes in subduction zones (for example for the 1960 Chile, 1966 Aleution, and 1969 Kuriles earthquakes) (Kanamori and Anderson, 1975). In our model the static stress drop for the hypothetical earthquake is 62 bars. In view of high ambient tectonic stresses a value of 100 bars is adopted for the sub-event stress drop (parameter). This parameter determines the relative distribution of energy among the higher and lower frequencies in the spectrum of the ground motion while the total energy radiated by the earthquake remains defined by the static stress drop. A higher value of the sub-event stress drop will cause the accelerogram to have higher frequency content and larger peak ground acceleration (pga) value while a lower value of stress drop will shift the energy to lower frequencies thereby lowering the pga. To examine the dependence of ground motions on this parameter simulations were also done for a value of 70 bars and an example for the case of Tehri is presented and the results are discussed.

In earthquakes the rupture starts at a localized place on the fault plane which is usually on the down dip edge of the fault plane. Two locations A and B were chosen to represent unilateral and bilateral ruptures for the case of Tehri site. This enabled us to study rupture propagation effects on the ground motions. As ruptures during earthquakes have the aspects of randomness several synthetic ground motions were generated to assess the variability of ground motion parameters.

Tehri Dam Site : A number of simulations were done, of which five examples of the expected strong ground motions for 100 bars stress drop are shown in Figures 4 and 5 for epicenters at A and B, respectevely. The accelerograms display the expected characteristics that the largest contributions to the ground motions come from the sections of the faults nearest to the station. The duration of the strong shaking (accelerations > 0.25 g) is about 60 s. This duration is the function of the fault size and is more or less the same in all the realizations. The envelopes of the accelero-

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grams also are similar in shape in various realizations. The peak accelerations which are high frequency phenomena exhibit a certain amount of variability in accordance with the random nature of the fault rupture.

The mean values and the standard deviations are shown in Table 2. The mean values of the peak ground accelerations (pga) for epicenter at A are (0.54 g (E-W); 0.78g (N-S); 0.84 g (Z)) and for the case of epicenter at B are (0.49 g (E-W); 0.97 g(N-S); 0.91 g(Z)). The E-W component is having smaller values as compared to the N-S component in accordance with the radiation pattern of the fault plane solution. The corresponding ground velocity time histories are also shown in the same figures. The velocity time histories have lower frequencies and show a strong pulse with dominant period of about 10 s for the case of epicenter at B while for epicenter at A there are three pulses of similar amplitudes. Besides there are 1s oscillations overriding the waveforms. The average figures of the peak ground velocities (pgv) for epicenter at A are (88 cm/s (E-W); 117 cm/s (N-S); 135 cm/s(Z)) and for the case of epicenter at B are (74 cm/s (E-W); 151 cm/s (N-S); 146 cm/s (Z)).

The Fourier and the 5% damping response spectra of the synthetic accelerograms are shown in Figs. 6 and 7 for epicenters at A and B respectively. The spectra show a corner at about 0.05 Hz which is consistent with the largest sub-event permitted in the simulation of the earthquake fault process. The slopes of the spectrum for frequencies below the corner frequency are consistent with the omega squared model. The 50th percentile value of the larger spectral acceleration for horizontal component (N-S) for epicenter at B at 0.4 s period is approxi- mately 2.6 g. This period corresponds to the single story houses and they will be exposed to extreme hazard. In the period range 1s to 2s in which large structures such as the Tehri dam which is under construction the spectral accelerations attain values between 2.1 and 0.85 g at the 84th percentile level.

The ground motion time histories for sub-event stress drop of 70 bars for the epicenter at B are shown in Fig. 8. The mean pga values somewhat smaller as compared to in the case of 100 bars stress drop and are (0.44 g (E-W); 0.71 g (N-S); 0.77 g (Z)).

The pgv values are (74 cm/s (E-W); 131 cm/s (N-S); 133 cm/s (Z)). The 5% response spectra and Fourier spectra are shown in Fig. 9. The average S_a (T) for period T of 0.4s is about 1.8 g, at 0.75 s is 1.8 g and at 1.25s is 1.2g. Thus for either choice of the sub-event stress drop the hazard levels are very high.

The waveforms in the above cases of sub-event stress drops have similar appearance although the 100 bar waveforms are generally richer in higher frequencies. This is a general finding observed at all the stations. Therefore the figures for the remaining stations are presented for the case of 100 bar stress drop only.

Dehradun Town : This is a prominent town having a population of about 300,000. The town is also a significant center for education, scientific research and military establishments. The site lies within the ambit

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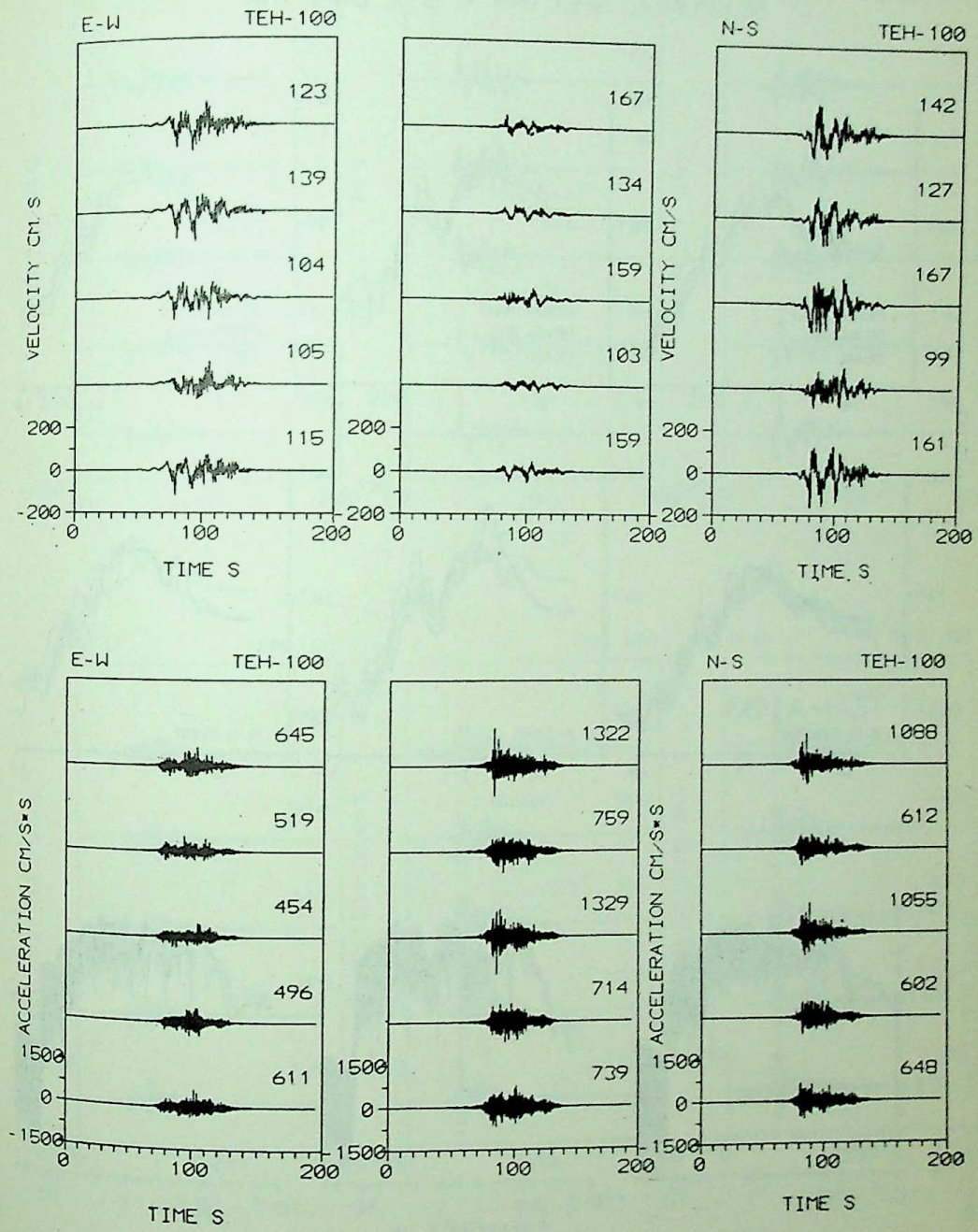

Fig. 4–Ground motion time histories for Tehri, Epicenter at A. Stress drop 100 bars.

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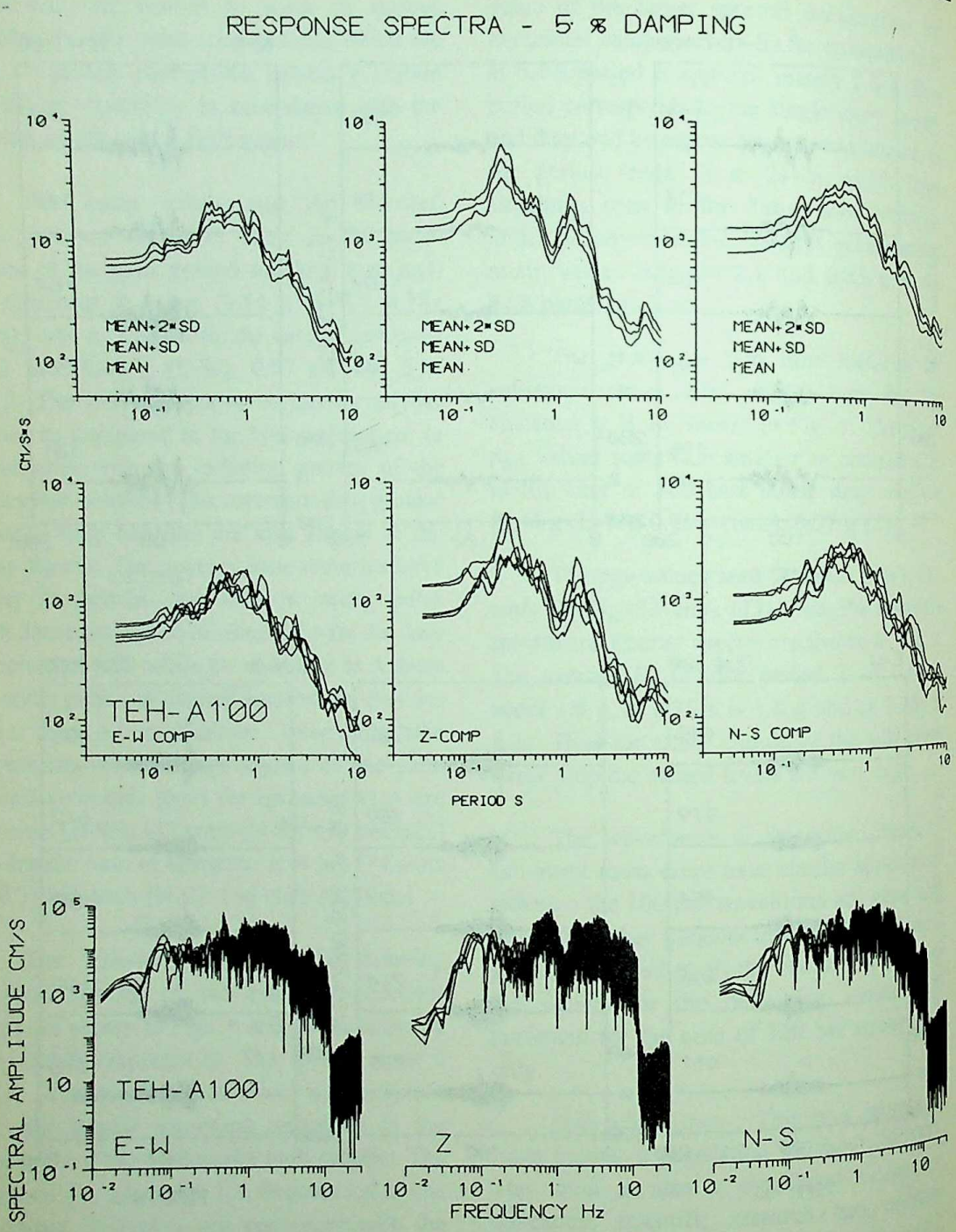

Fig. 5–5% damping response spectra and Fourier spectra for Tehri A : 100 bars.

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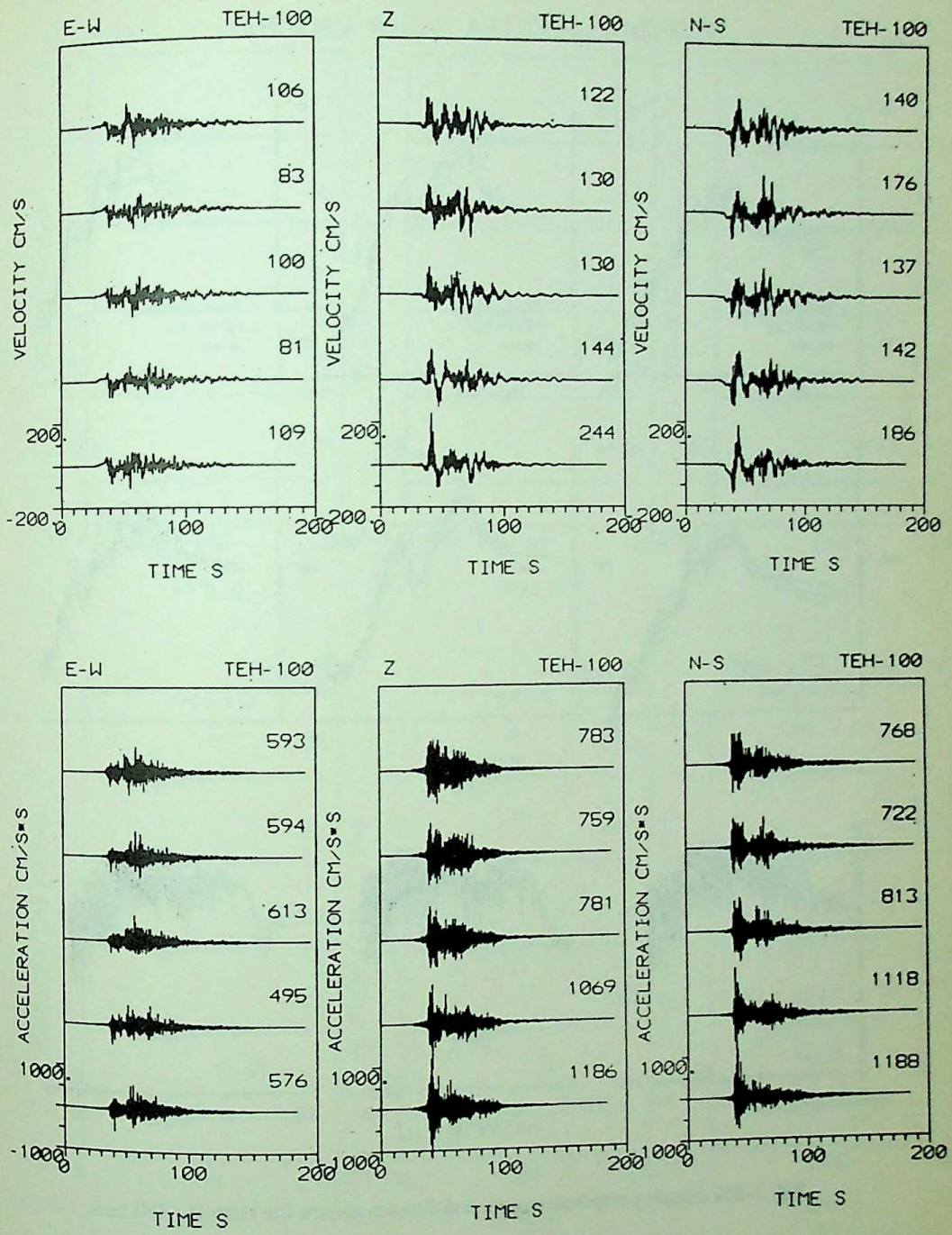

Fig. 6–Ground motion time histories for Tehri, Epicenter at B. Stress drop 100 bars.

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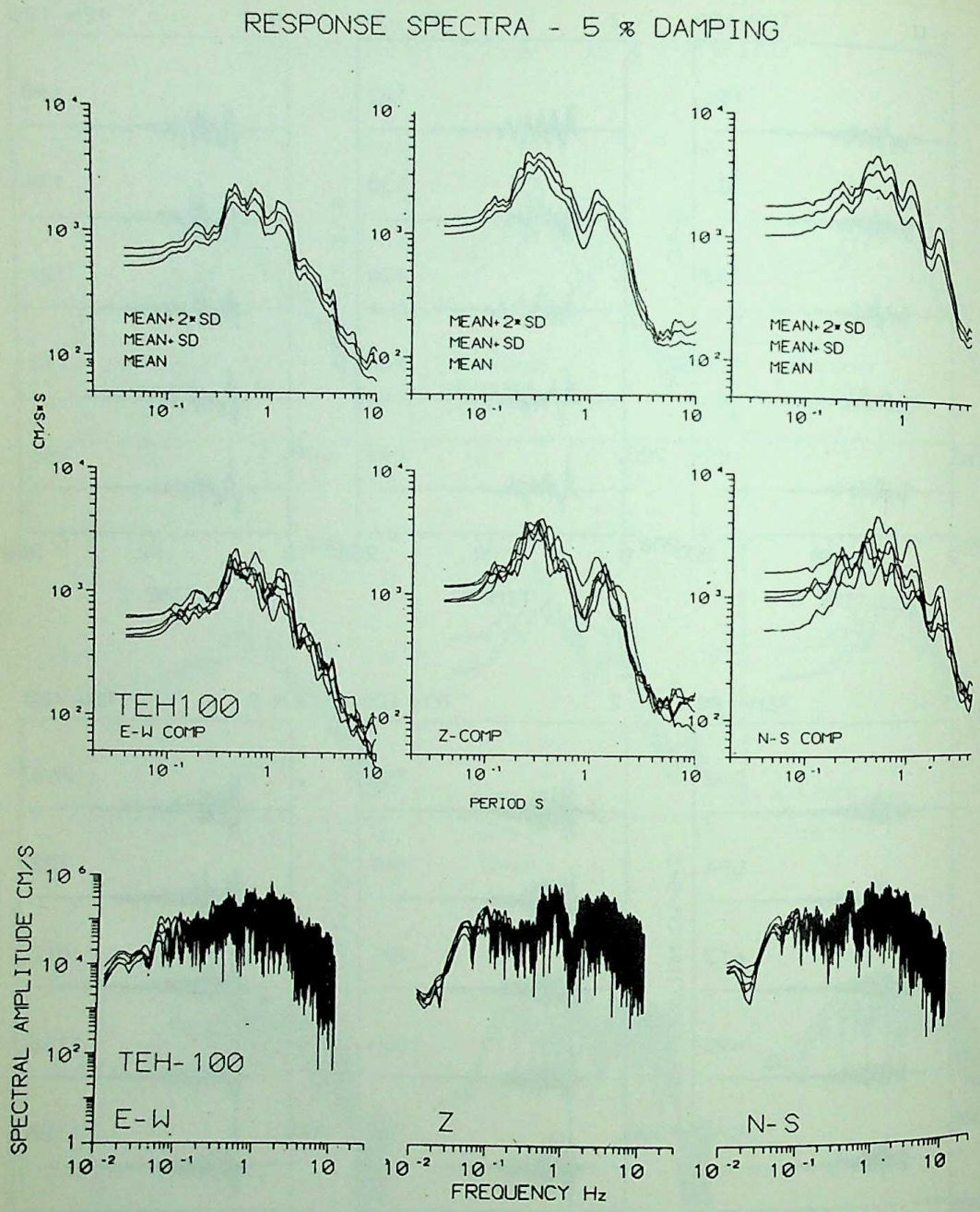

Fig. 7–5% damping response spectra and Fourier spectra for Tehri B : 100 bars.

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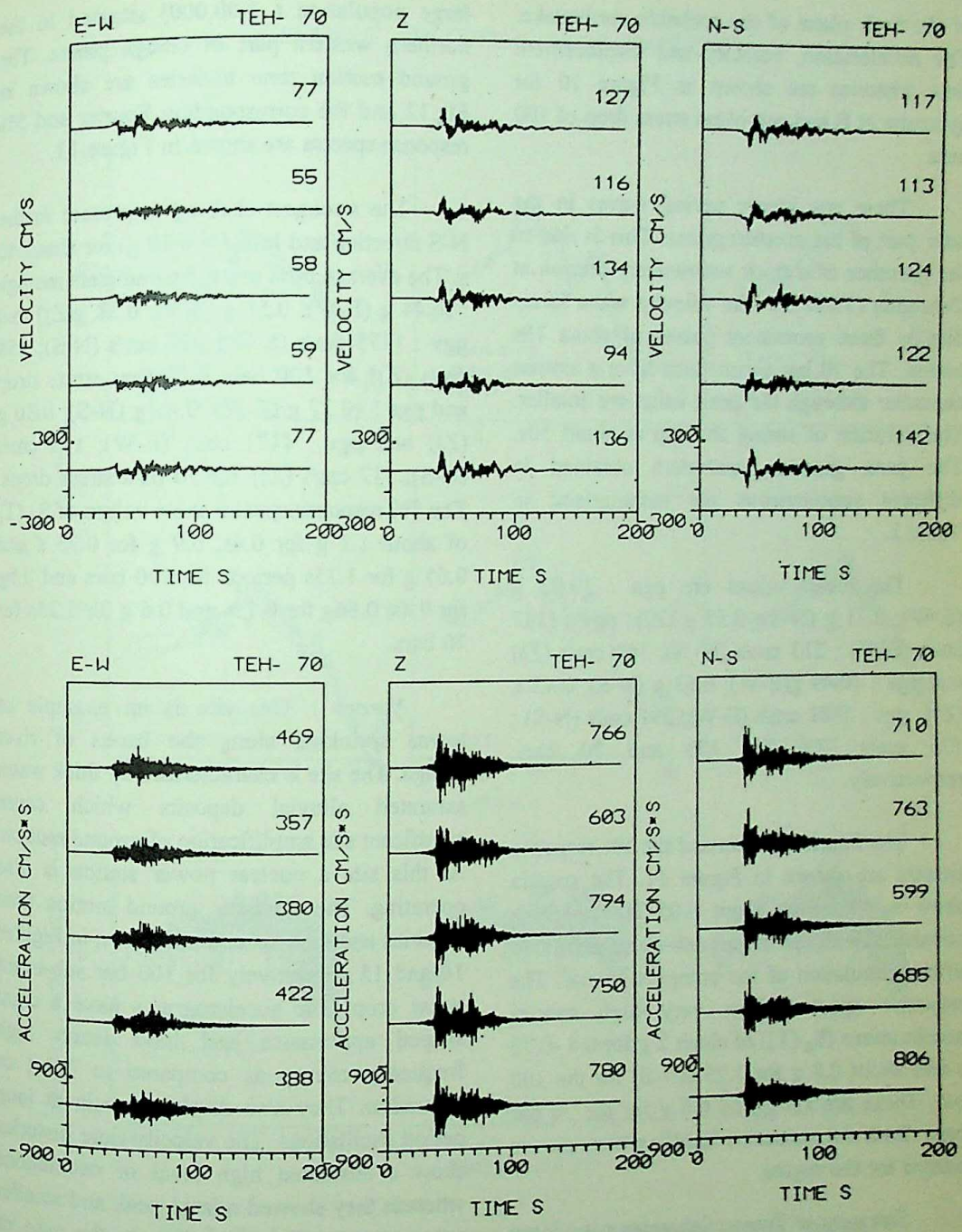

Fig. 8–Ground motion time histories for Tehri, Epicenter at B. Stress drop 70 bars.

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of the fault plane of the probable earthquake. The acceleration, velocity and displacement time histories are shown in Figure 10 for epicenter at B and sub-event stress drop of 100 bars.

There are longer period waves in the later part of the accelerograms. This is due to the presence of a thick sedimentary section at Dehradun (Table 1). The velocity wave forms display three prominent pulses of about 10s period. The 70 bar simulations have a similar character although the peak value are smaller. The duration of strong shaking is about 50s. The peak ground parameters obtained in different simultaneous are summarized in Table 2.

The mean values are pga : {0.07 g (E-W); 0.71 g (N-S); 0.55 g (Z)}; pgv : (187 cm/s (E-W) : 213 cm/s (N- S); 149 cm/s (Z)) and pga : {0.49 g(E-W); 0.63 g (N-S); 0.43 g (Z)}; pgv : {188 cm/s (E-W); 231 cm/s (N-S) : 135 cm/s (Z)} for 100 and 70 bars, respectively.

The Fourier spectra and the 5% response spectra are shown in Figure 11. The spectra show a corner at about 0.05 Hz which is consistent with the largest sub-event permitted in the simulation of the complex source. The response spectra show very high spectra accelarations (S_a (T)) of about 2 g for 0.4 -0.75 s and about 0.8 g for 1.25 s(N-S) for the 100 bar. These are 1.2 g and 0.6 g for the 70 bar case. Both the scenarios signify a very severe hazard for the region.

Saharanpur Town : Saharanpur is a large town and a developing industrial center with a large population (3,00,000) situated in the northern western part of Ganga plains. The ground motion time histories are shown in Fig.12 and the corresponding Fourier and 5% response spectra are shown in Figure 13.

The strongest shaking is present in the N-S direction and lasts (> 0.15 g) for about 40 s. The average peak ground parameters are pga : (0.44 g (E-W); 0.51 g (N-S); 0.38 g(Z)) and pgv : {175 cm/s (E-W); 127 cm/s (N-S); 158 cm/s (Z)} for 100 bars sub-event stress drop and pga : {0.37 g (E-W); 0.45 g (N-S); 0.30 g (Z)} and pgv : {171 cm/s (E-W); 114 cm/s (N-S); 112 cm/s (Z)} for 70 bars stress drops. The 5% response spectra show values of S_a (T) of about 1.1 g for 0.4s, 0.9 g for 0.75 s and 0.65 g for 1.25s periods for 100 bars and 0.9g for 0.4s, 0.66g for 0.75s and 0.6 g for 1.25s for 70 bars.

Narora : This site is an example of towns sprinkled along the banks of river Ganga. The site is characterized by thick water saturated alluvial deposits which cause significant site amplification of ground motion. At this site a nuclear power station is also operating. The synthetic ground motion time histories and their spectra are shown in Figures 14 and 15 respectively for 100 bar sub-event stress drop. The accelerograms have a cigar shaped appearance and have lesser high frequency energy as compared to Tehri or Dehradun. They also display prominent long period oscillations. The velocity time histories show a sustained high level of oscillations whereas they showed a large peak and smaller subsequent oscillatory motion in the case of Tehri and Uttarkashi both of which lie with in

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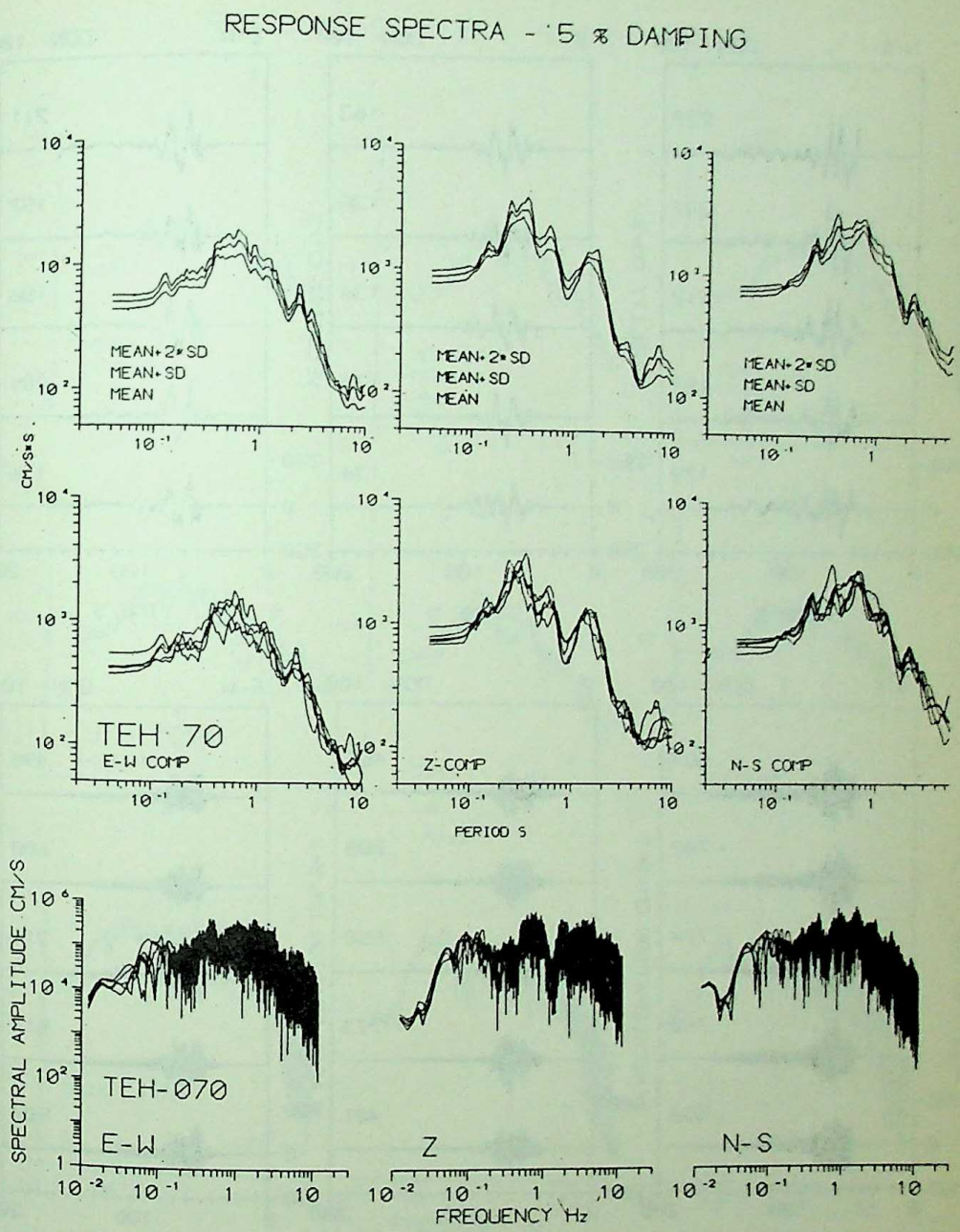

Fig. 9–5% damping response spectra and Fourier spectra for Tehri B : 70 bars.

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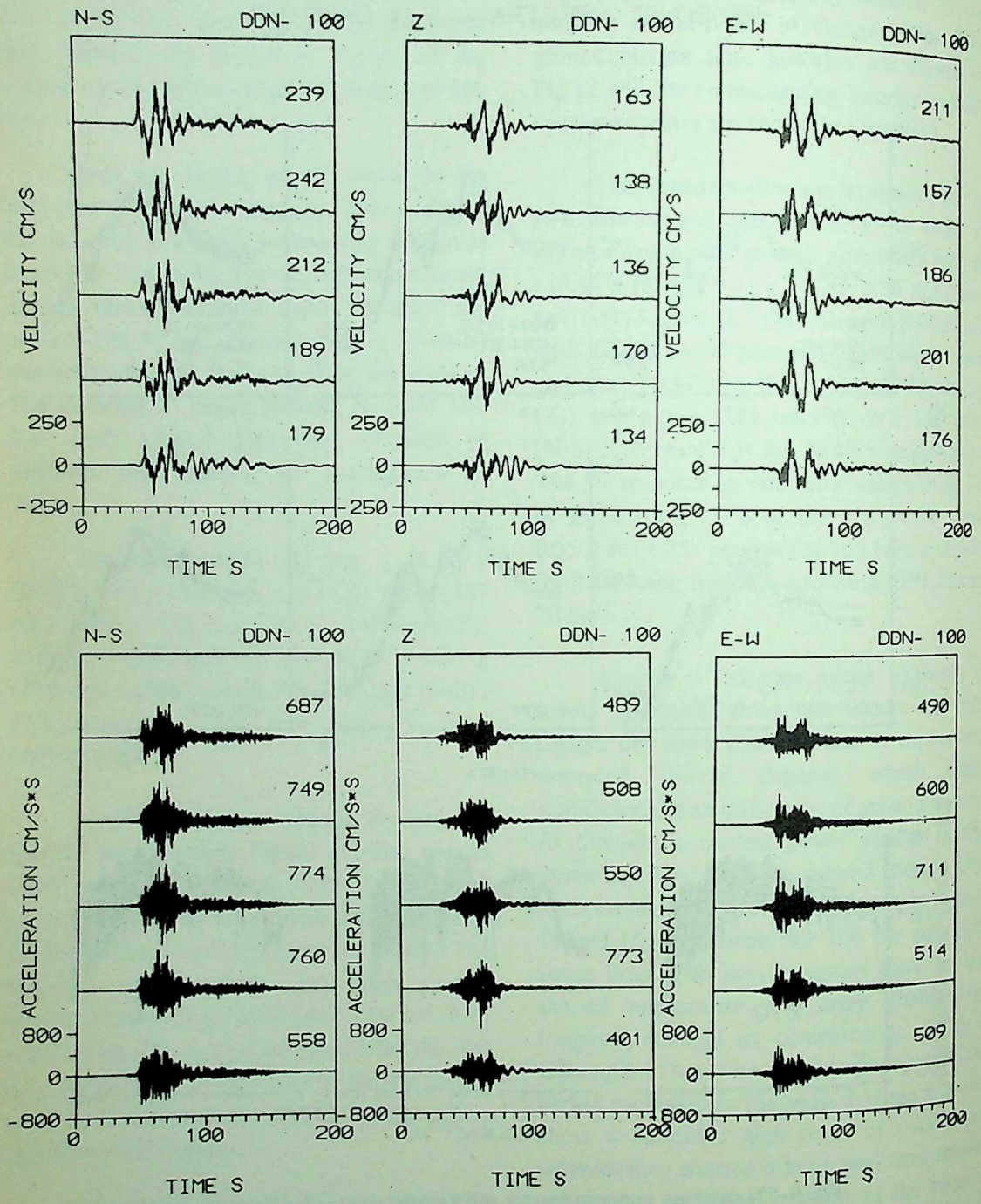

Fig. 10–Ground motion time histories for Dehradun, Epicenter at B. Stress drop 100 bars.

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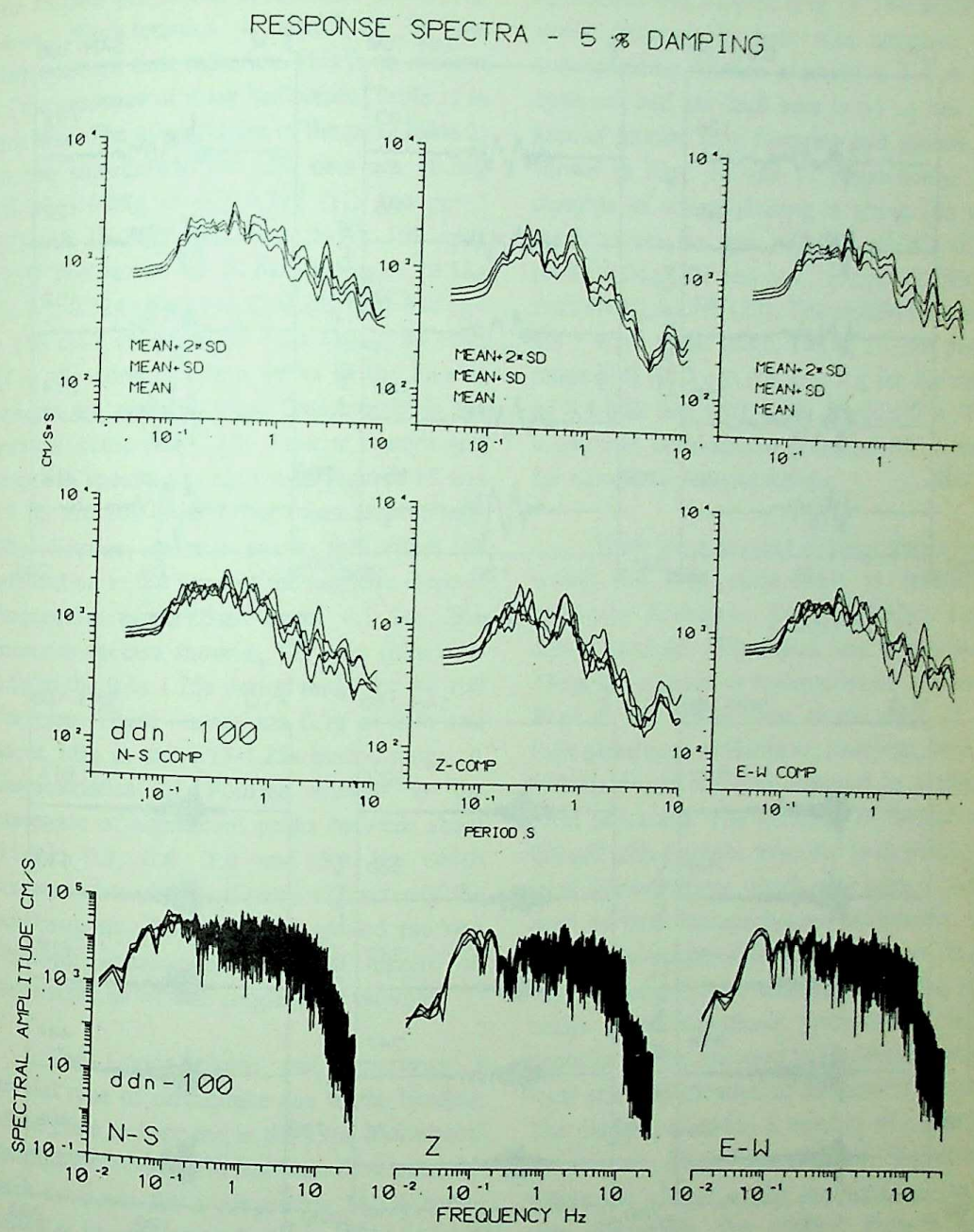

Fig. 11–5% damping response spectra and Fourier spectra for Dehradun B : 100 bars.

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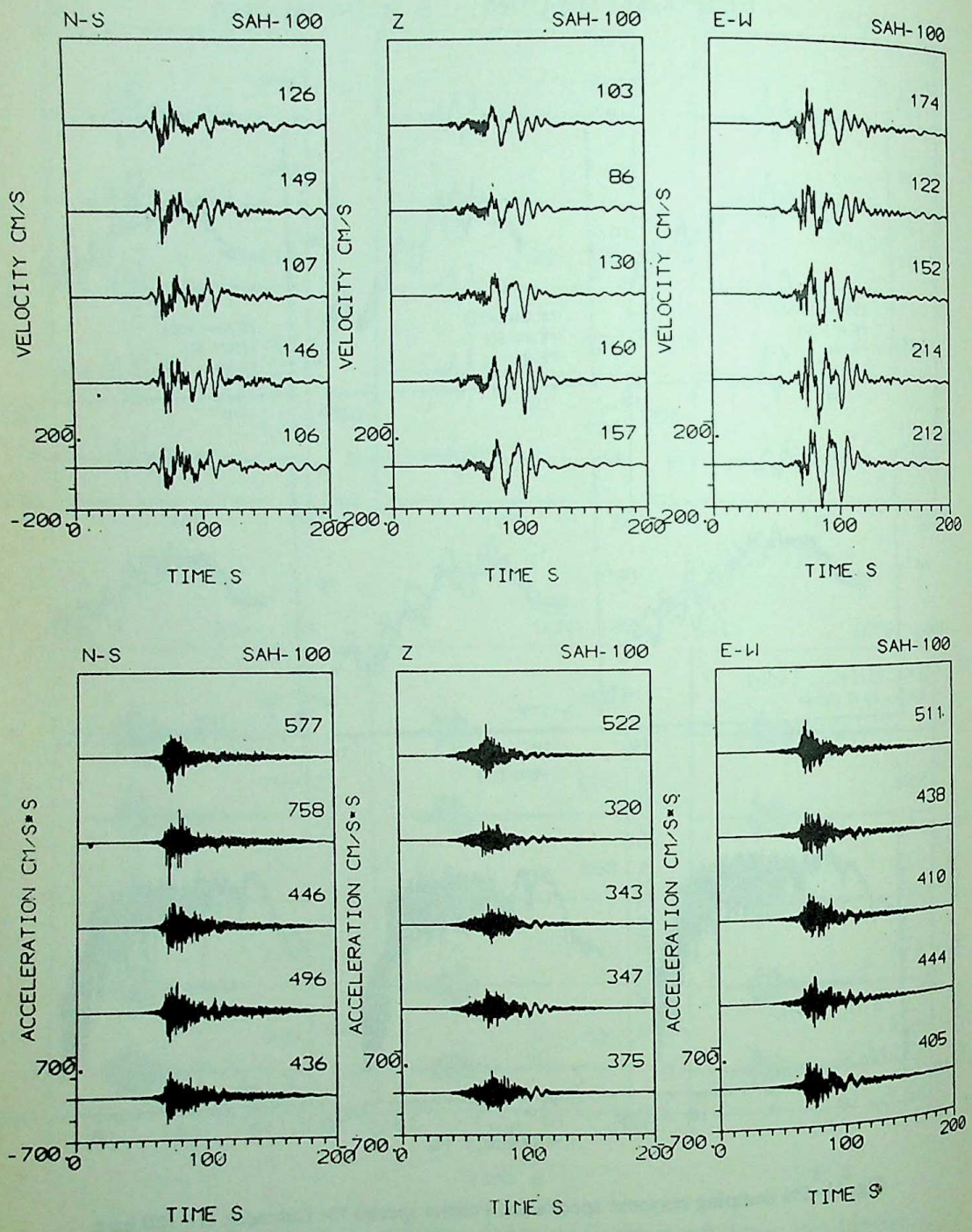

Fig. 12–Ground motion time histories for Saharanpur, Epicenter at B. Stress drop 100 bars.

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the surface projection of the fualt plane. The same characteristics is displayed by the displacement time histories. This is on account of the presence of thick sediments (Table 1) in this area. The mean values of the pga (Table 2) in the simulations for 100 bars are {0.26g (E-W) ; 0.48g (N-S); 0.27g (z)} and pgv : {73cm/s (E-W); 150 cm/s (N-S); 109 cm/s (Z)}. The values for 70 bars are pga : {0.18g (E-W); 0.32g (N-S) (N-S); 0.23g (Z)} and pgv : {56 cm/s (E-W); 109 cm/s (N-S); 88 cm/s (Z)}. the corresponding peaks in the Fourier spectra are present, more prominently in the vertical component. The Fourier spectra and response spectra are shown in Figures 18 and 19 for the 100 and 70 bar cases respectively. The Fourier spectra show the effect of attenuation in the form of the negative slope at frequencies larger than about 0.1 Hz. The response spectra show S_a (T) of a little over 1.0g in the 0.4s 1.25s period range for the 100 bar case. These values are 0.9g at 0.4s and about 1.0g in the 0.75-1.25s period range. A characteristics of Fourier spectra is the presennce of significant peaks between about 0.1-0.2, 0.3, 0.6, 3.0 and 8.0 Hz which correspond to the oscillatory character of the accelerogrms. The expected ground motions represent considerable leve of hazard to multi-story as well as single-story building.

The Ganga plains can experience a normal type of earthquake due to the bending of the plate as happend in the 1966 Moradabad earthquake. A scenario has been developed for such an event for a magnitude M_w 6 earthquake at an epicentral distances of 11 km due N30°E from Narora and at a depth of 44 km. The fault plane solution of the Moradabad earthquake was adopted (Fig 1). The sub-event stress drop of 70 bars was adopted. The corresponding seismic moment is 1.4×10^{25} dyne cm and the fault area is 64 sq km. The ground motion time histories and spectra are shown in Figs. 16 and 17 respectively. The duration of strong shaking is about 10s with mean values for pga : {0.07g (E-W); 0.37g (N-S); 0.04g (Z)} and pgv : {7cm/s (E-W); 32 cm/s (N-S); 3 cm/s (Z)}. The station is close to the P wave nodal plane. The S_a (T) for period range of 0.1-0.3 s is 0.8 g; 0.5 g for the range of 0.4-0.8s and 0.07 g for about 1.2 s. This constitutes considerable potential for damage for normal civil constructions.

There are a number of large towns lying within the fault plane such as Dehradun, Mussorie, Rishikesh, Tehri, Srinagar, Lansdown, Ranikhet, Pithoragarh, and Champawat. These are exposed to extreme levels of hazard. Besides, the towns close to the edge of the fault plane such as Hardwar, Kotdwar, Nainital and Haldwani are also exposed to a similar level of hazard. The intensity of hazard will fall off with distance from the fault plane, but local site conditions which may have a pile of near surface unconsolidated sediments will have consi- derable hazard as shown in the case of Narora. Such sites will be along river banks where significant thickness of recent deposits will be expected to be present causing local site amplification of the ground motions. The Ganga plains has a number of cities like Saharanpur, Mujjafarnagar, and Moradabad, where the effects of the earthquakes can be very damaging. The disaster from a great earthquake can be tremendously intensified by the failure of a facility like a large dam by the

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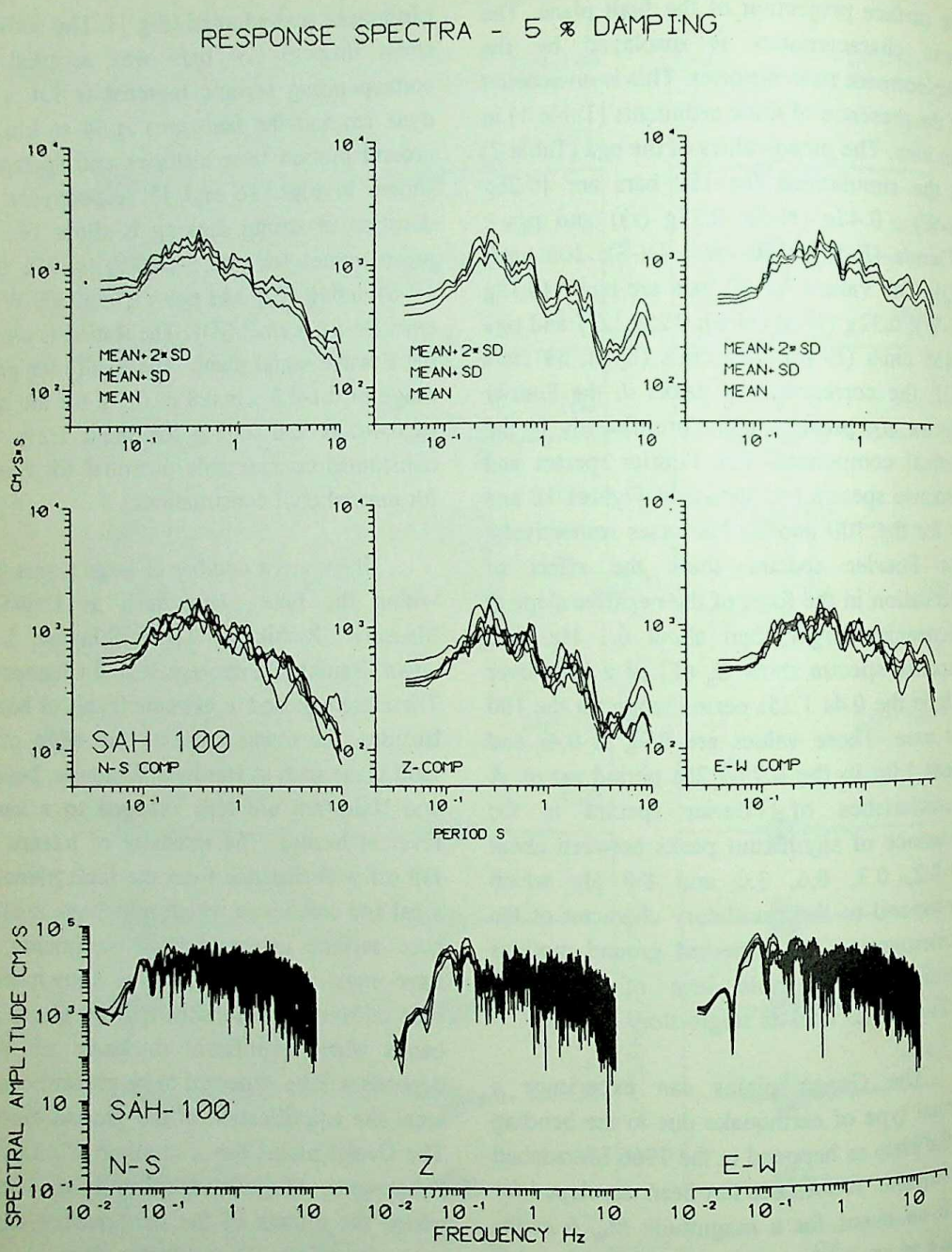

Fig. 13–5% damping response spectra and Fourier spectra for Saharanpur B : 100 bars.

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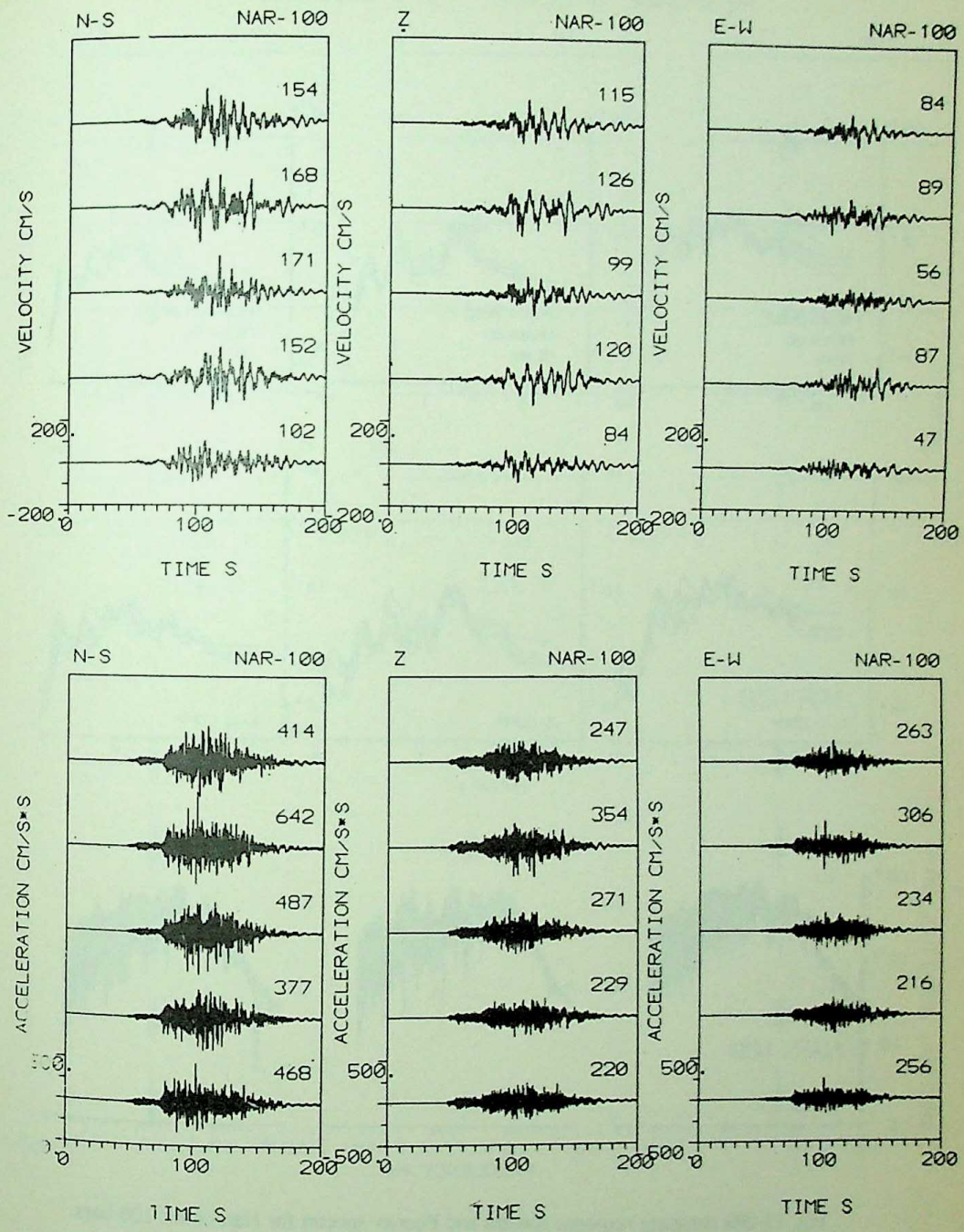

Fig. 14–Ground motion time histories for Narora. Epicenter at B. Stress drop 100 bars.

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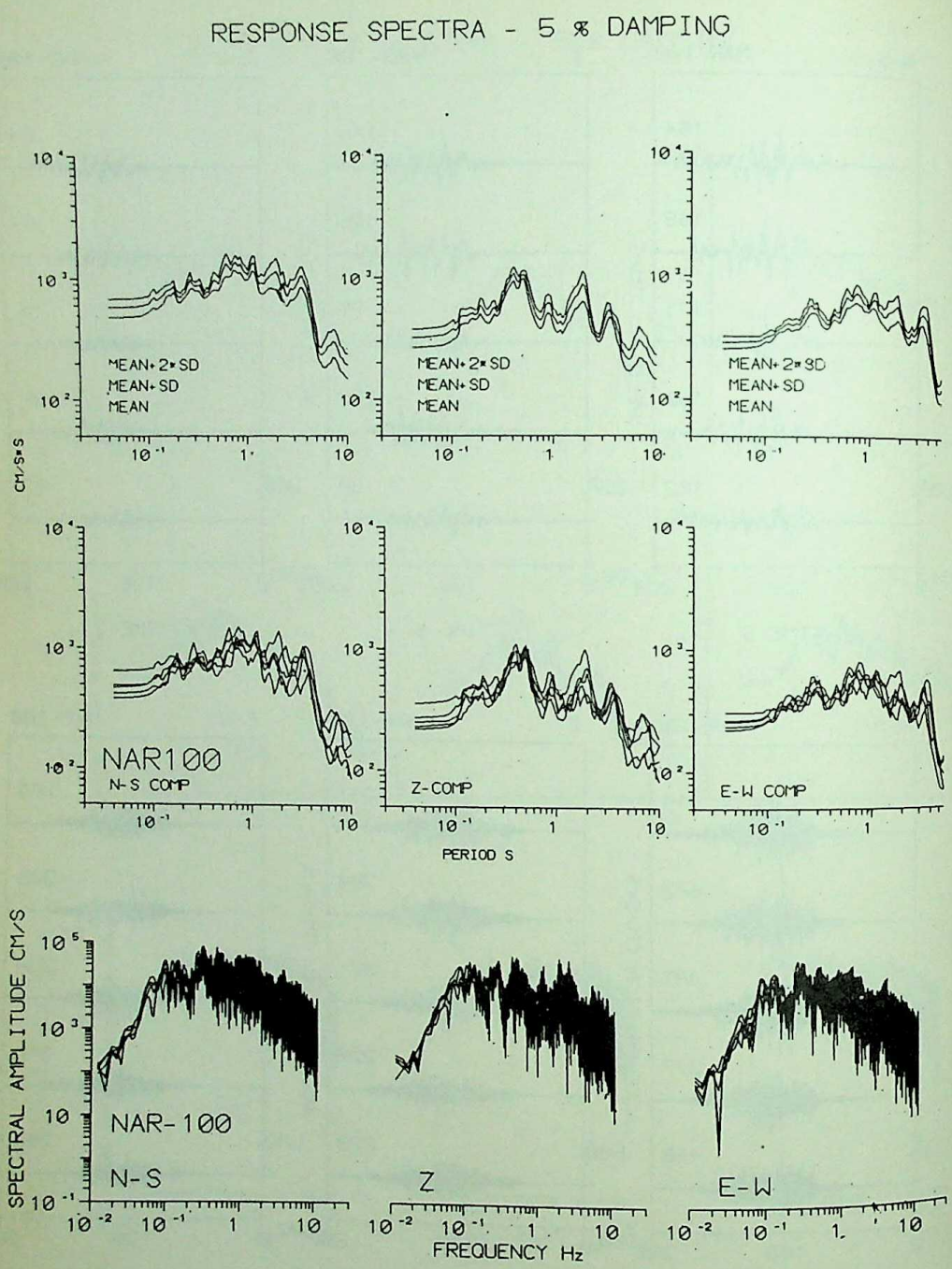

Fig. 15–5% damping response spectra and Fourier spectra for Narora B : 100 bars.

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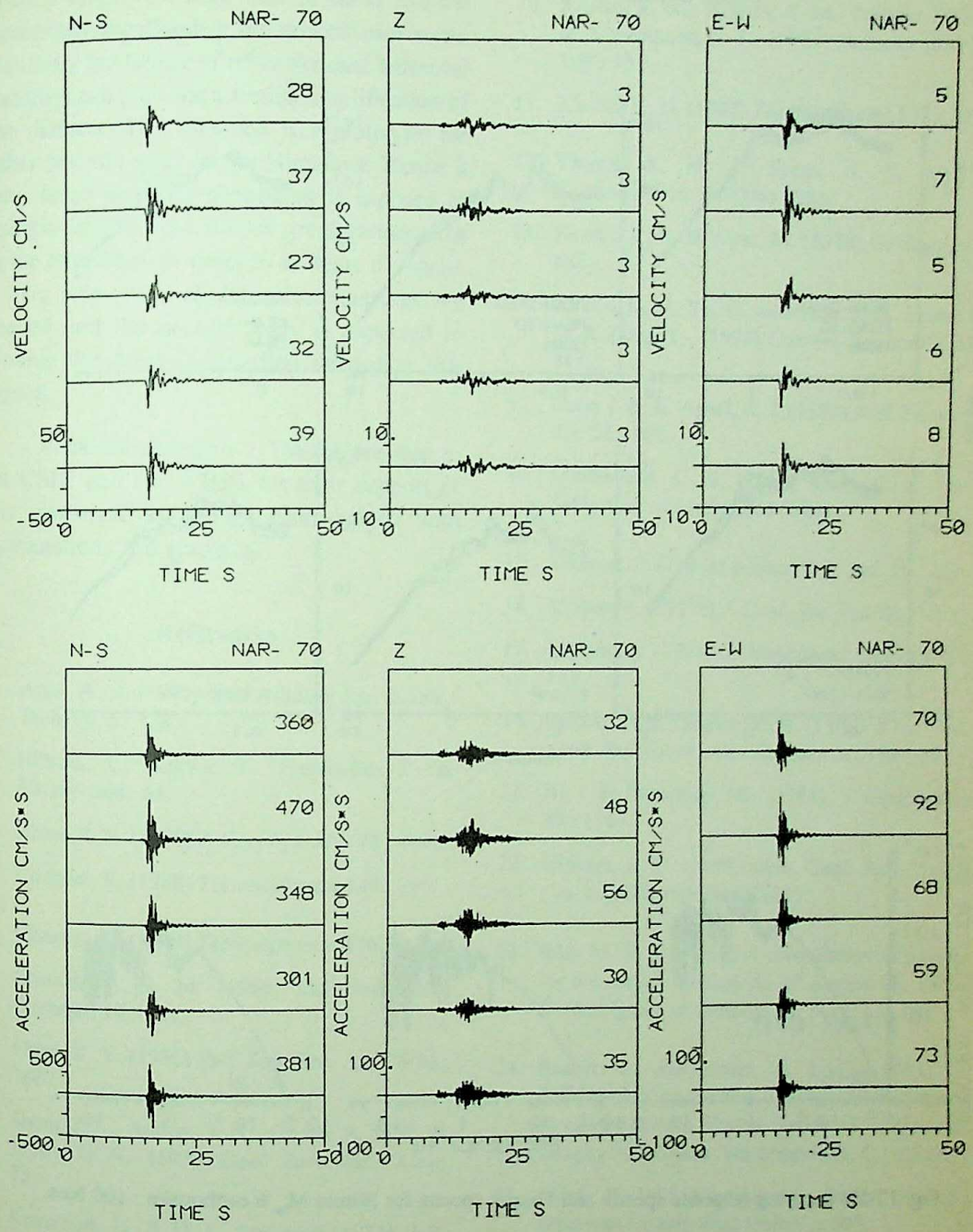

Fig. 16–Ground motion time histories for Narora for M earthquake at an epicentral distance of 14 km : stress drop bars.

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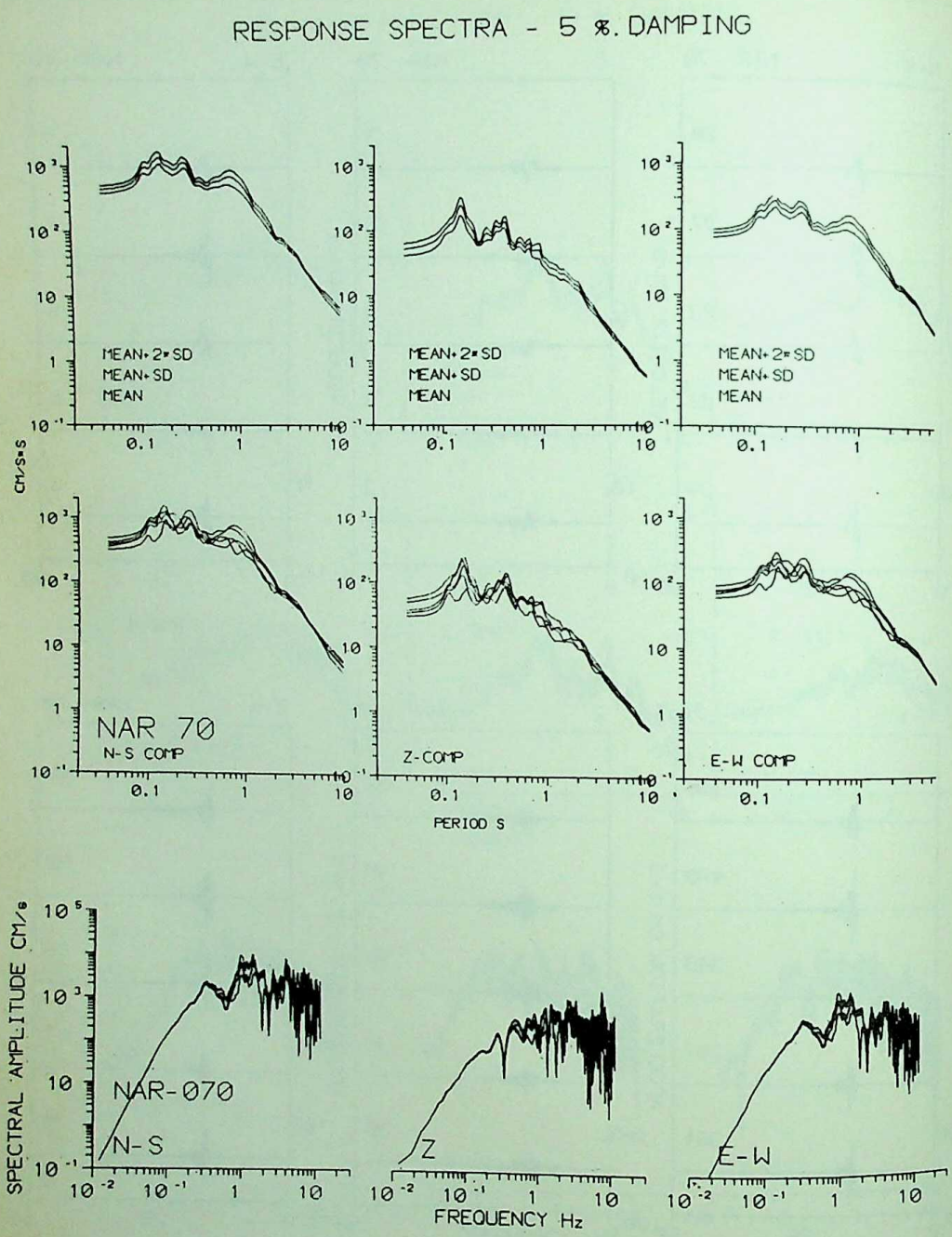

Fig. 17 5% damping response spectra and Fourier spectra for Narora M_w 6 earthquake : 100 bars.

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instant surge of a high wall of water and the accompanying flood in the downstream areas. Similarly the failure of other toxicant industrial facilities can provoke a similar amplification of the disaster. This situation is a prototype for other seismic gaps in the Himalaya. Hence a very large area and population is exposed to seismic hazard from future great earthquakes in the Himalaya. In order to mitigate the same, a long term plan of defensive measures are needed and the present study is expected to provide the basic information needed in this regard.

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Earthquakes can be predicted

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Abstract : Earthquakes are the results of sudden fault motion that are due to plate motion and their short-term prediction is difficult. However, earthquake prediction has been in practice in Greece for more than a decade by the so called VAN method. The method is based on detection of characteristic changes in the geoelectric potential that appear prior to earthquakes. Some promising indications have been obtained also in Japan.

(**Keywords** : earthquake prediction / VAN method)

What are Earthquakes : Earthquakes are the results of sudden fracture taking place in earth in the form of fault motion. Fracture in the earth does not take the form of explosion or implosion. It makes blocks slide along faults.

There are three typical geometrically possible fault motions (Fig.1). One is divergent : when a block is pulled from both sides, it splits into two along an inclined plane called a normal fault plane. If it is pushed from both sides, the fault motion is convergent, forming what is called a thrust or reverse fault. And when the blocks slide horizontally, a strike-slip or lateral slip fault is formed. Earthquakes are caused by such fault motions. This is a conclusion derived from many years' study of seismologists.

Earthquakes do not occur everywhere, but at certain specific places that form more or less linear zones. As seen in Fig. 2a, most of earthquakes occur along the Pacific rim subduction zones and collision zones like the Himalayas. Many other small earthquakes occur along the undersea ridges, namely the mid-oceanic ridges. These earthquakes are called inter-plate earthquakes as they occur along the boundaries between plates that cover the surface of the whole earth and are in constant motion. The Pacific plate, the fastest plate, for instance, is moving northwestward with a speed of about 10 cm per year. Plate motions result in global scale migration of continents and oceans in the geologic time. There are some earthquakes that occur not at plate boundaries like those occurring in Eurasian and American continents. They are called intra-plate earthquakes.

Depth of most earthquake foci is shallow, say less than 20 km depth. Earthquakes with deeper foci, the deep earthquakes, occur only along the subduction zones (Fig.2b), with a notable exception of Hindu Kush area.

Above-mentioned three types of fault motions, i.e., earthquakes, are characteristic to

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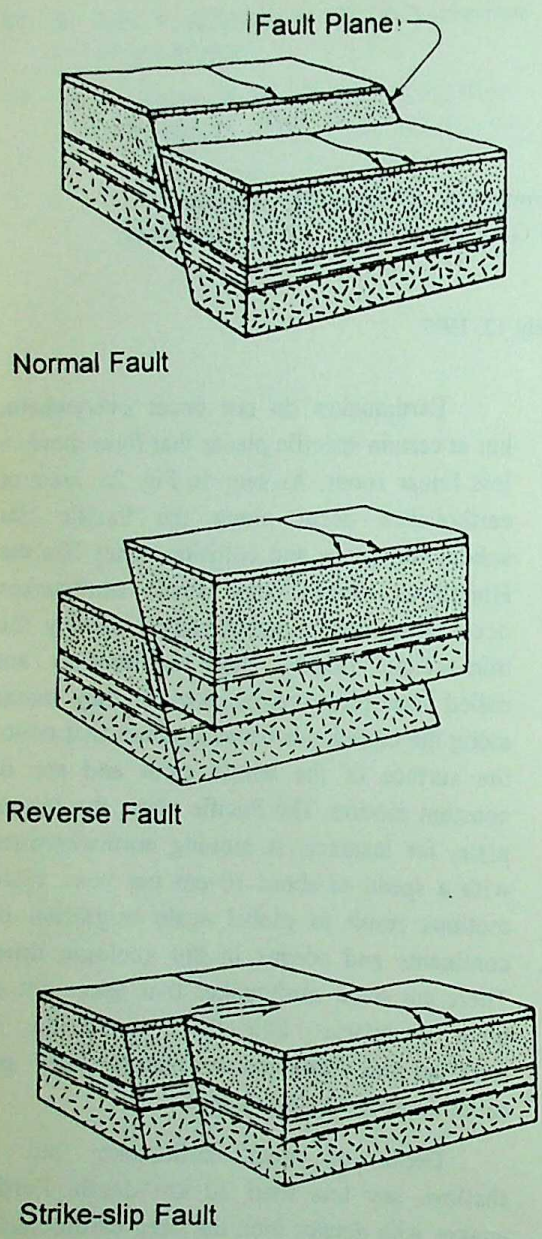

Fig. 1–Three types of fault, from top to bottom, Normal fault, Reverse fault and Strike-slip fault.

three corresponding types of plate boundaries (Fig. 3). The diverging type earthquake takes place under the seafloor spreading center (mid-oceanic ridges) where sea floor is generated and stretched to spread (b). The converging, or pushing type earthquake takes place where two plates meet or one of them goes underneath the other, namely the subduction zones like Japan (a_1). and collision zones like Himalayas (a_2). The biggest earthquakes occur in subduction zones and collision zones. The third type is called the transform boundary (c) where two plates move sideways like the San Andreas Fault in California.

Plates move because of the convection in the mantle, the thermal convection. This idea has long been not more than a speculation, but nowadays it is becoming a knowledge, thanks to the progress of a branch of seismology called seismic tomography. Analyzing millions of records of seismic wave propagation, in a manner analogous to the X-ray CT scan in medical science, seismologists can obtain three dimensional images of the distribution of seismic wave velocity in the earth's mantle. Such images show remarkable patterns that can be interpreted as a result of thermal convection (Fukao *et al.* 1992). The mantle convects because of the cooling process of the earth.

Earthquake Prediction : Although many things are now known about earthquakes, to predict their occurrence is difficult. To predict earthquakes, it is essential but to provide three basic elements of information of the impending earthquake, i.e., where, when and how large it is going to be, with precision useful to human society.

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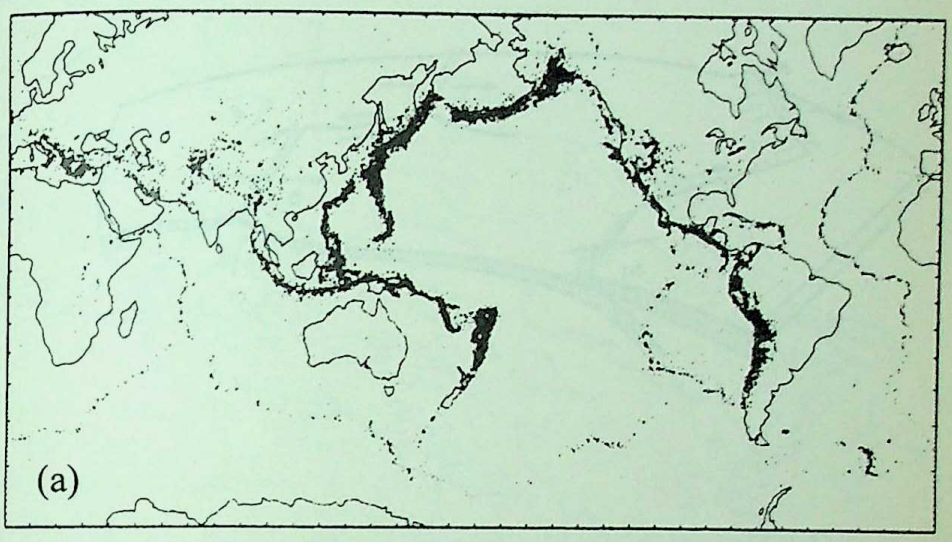
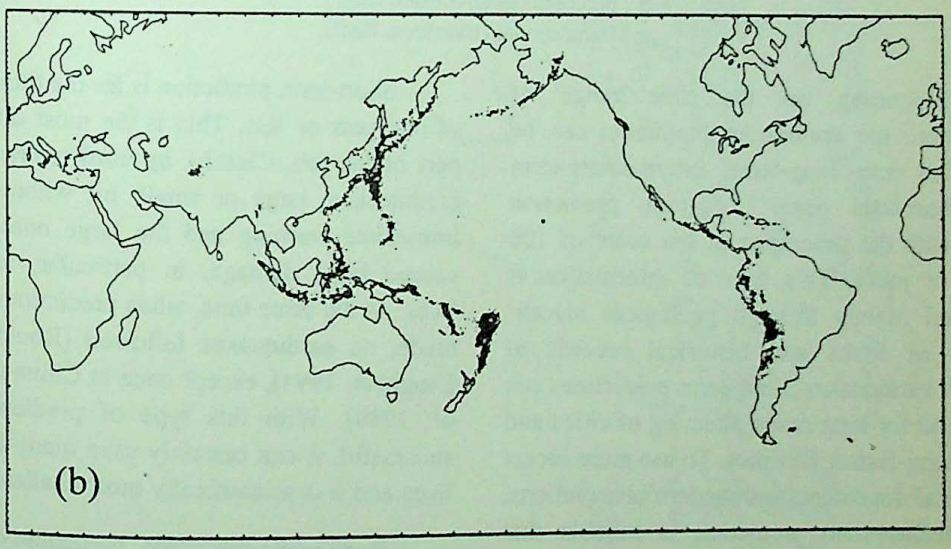


(a) Events with focal depths between 0 and 700 km.



(b) Events with focal depth deeper than 100 km.

Fig. 2–Distribution of earthquake epicenters (U. S. Coast and Geodetic Survey)

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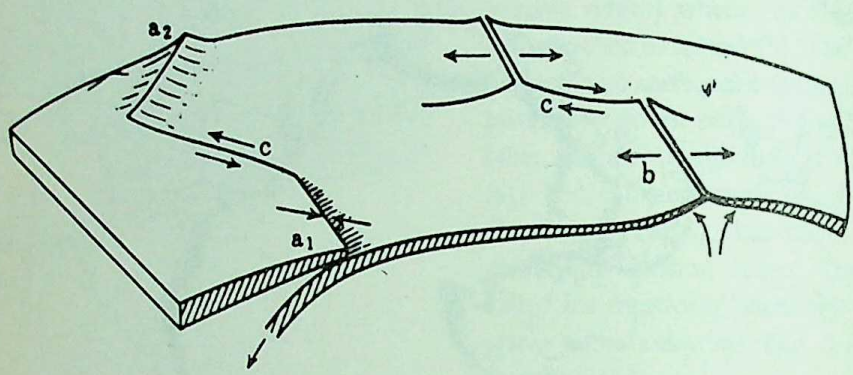

Fig. 3–Three types of plate boundary.

a : convergent (a_1 subduction zone, a_2 : collision zone)
b : divergent (mid-oceanic ridge)
c : translational (transform fault)

Depending on the time range of prediction, the earthquake prediction can be classified into long-term, intermediate-term and short-term ones. Long-term prediction deals with the time span of the order of 100 years or more. This type of information is obtained mainly through geological investigation of faults and historical records of ancient earthquakes. Long term predictions can be useful for long range planning of cities and other long-lasting facilities. To use more recent historical documents and modern observations, intermediate-term prediction is suitable that concerns the time span of the order of 10 years or so. Intermediate-term predictions have been successful in few cases (Lomnitz, 1994), but it has often failed (Wyss & Baer, 1981).

Short-term prediction is for the time span of one year or less. This is the most difficult part of the job. Clearly, up until today, most earthquakes, large or small, hit without any immediate warning and the large ones have caused huge damage, in particular, loss of lives. At the same time, when predictions were made, no earthquakes followed (Roeloffs & Langbein, 1994), except once in China (Ma *et al.* 1989). With this type of prediction, if successful, it can certainly save many human lives and it is scientifically most challenging.

Earthquake prediction, particularly short-term one, is somewhat analogous to predicting changes in the exchange rate or stock market. Analogous because both are virtually out of ones control, once it starts it proceeds rapidly

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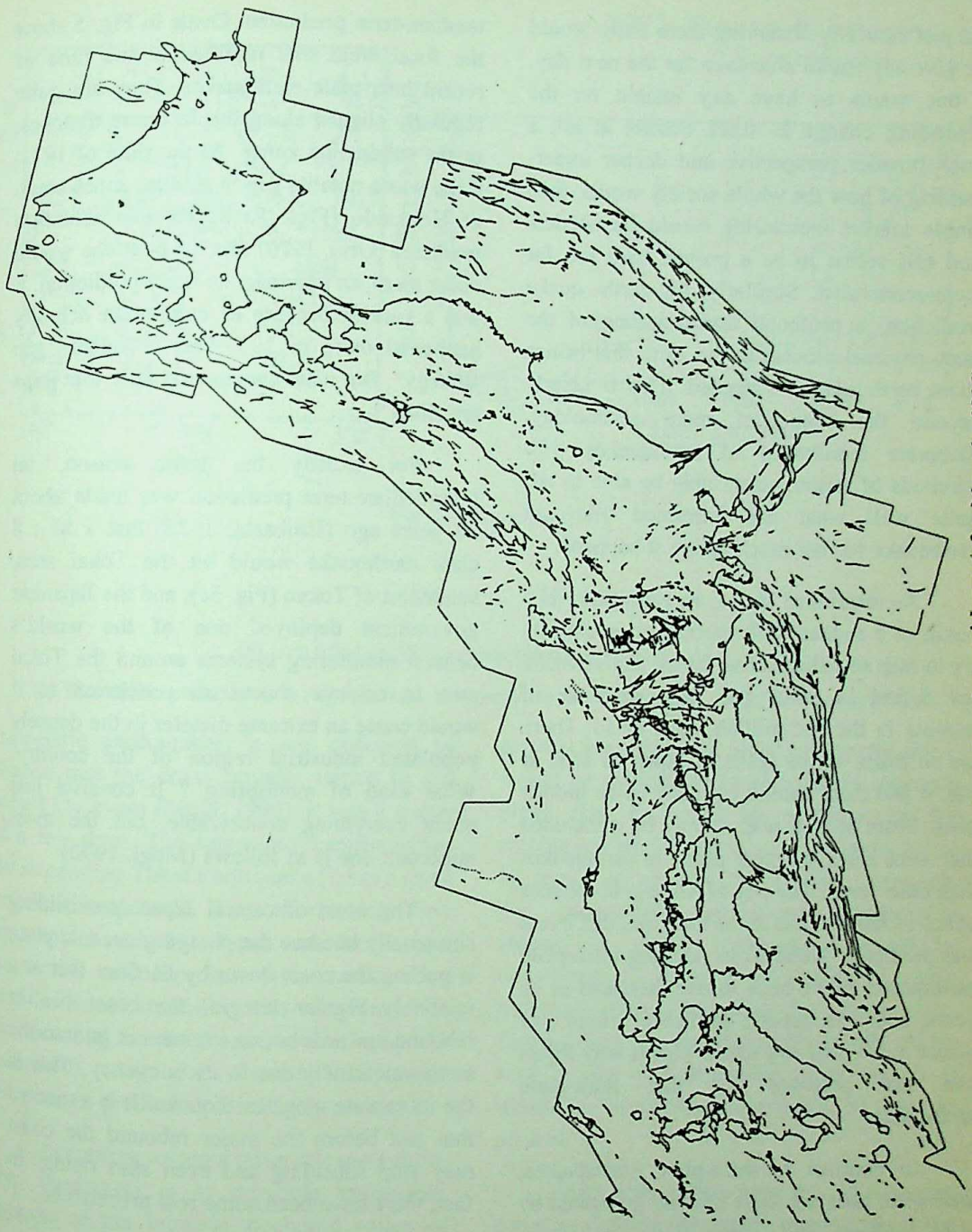

Fig. 4–Active faults in and around Japan (after Matsuda, 1995).

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and just carefully observing them daily would not give any useful clue even for the next day. If one wants to have any insight on the impending change in stock market at all, a much broader perspective and deeper understanding of how the whole society works, then simple market monitoring would be needed. And this seems to be a proven hard job for socio-economists. Similarly, for earth- quake prediction, a profound understanding of the basic physical process in the earth that brings about earthquakes, is needed. This is clearly beyond the scope of mere seismology. Elaborate monitoring of earthquakes with hundreds of seismometers may be able to tell quite well what has happened after an earthquake but not much before it happens.

As mentioned above, an earthquake is a result of a sudden fault motion, so geologists try to map so-called active faults. Active faults are defind as faults that have evidence of moving in the last million years or so. There are so many active faults in Japan as seen in Fig. 4 and there should be many more hidden ones. From such a map it may be concluded that some areas are more prone to earthquakes than other areas. The city of Kobe is in the area of active faults. Thus in the long run, that event was predicted. These faults, causing intra-plate earthquakes move once in one thousand or so years, and it is beyond prediction which one would move next and when. This is why Japan was not prepared for that intra-plate earthquake.

In contrast to intra-plate earthquakes, inter-plate ones are more directly generated by plate motions and occur more frequently, persumably giving better chance for intermediate-term prediction. Ovals in Fig. 5 show the focal areas that ruptured at the time of recent inter-plate earthquakes. They are quite regularly aligned along the Japanese trenches, or the subduction zones. At the time of 1972, there was a notable gap in rupture zones south of Hokkaido (Figs. 5a & 5b) and scientists predicted (Utsu, 1970) that the next one would occur there, an intermediate- term prediction. It was a success because an earthquake actually happened there in 1973.This is called "gap strategy". But what can be said after that gaps are filled ?

For exactly the same reason, an intermediate-term prediction was made about 20 years ago (Ishibashi, 1976) that a M : 8 class earthquake would hit the Tokai area, southwest of Tokyo (Fig. 5c), and the Japanese government deployed one of the world's densest monitoring systems around the Tokai area to achieve short-term prediction as it would cause an extreme disaster in the densely populated industrial region of the country. What kind of monitoring ? It consists just about everything conceivable, but the most important one is as follows (Mogi, 1990).

The coast of central Japan is subsiding chronically because the plunging oceanic plate is pulling the coast down by friction. But at a relatively regular interval the coast has to rebound upwards because it can not go into the earth indefinitely due to its buoyancy. This is the inter-plate mega-earthquake. It is expected that just before the major rebound the coast may stop subsiding and even start rising. In fact, there have been some real precedents.

In the cases of 1944 and 1946 major

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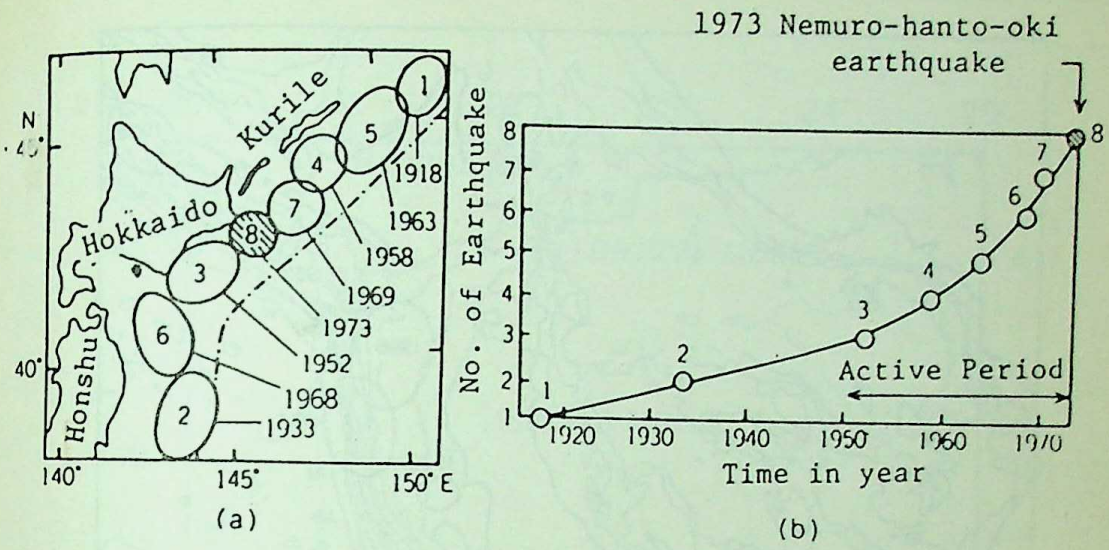

Fig. 5–Seismic gaps.

(a) (b)

(a) Gap filled by 1973 earthquake south of Hokkaido.

(b) Plot of the earthquakes (a) against time, that predicted the 1973 earthquake (after Mogi, 1977).

inter-plate earthquakes, it was observed by chance that the coast actually started to rise before the event (Mogi, 1990). It was a matter of a few days. The same may happen before the impending Tokai Earthquake (it has a name before it happens !). But, unfortunately there are many cases both in Japan and other parts of the world, such a precursor was not detected despite dense monitoring network. Thus, it is not sure that short-term prediction would be successful or not even for the Tokai quake. Short-terms prediction is certainly no easy.

According to some other scientists short-term prediction is in principle impossible, because of the intrinsic stochastic nature of fracture (Geller, 1991 : 1994). As if, a glass bar is to be broken by bending, it would be easy to say that it would break soon, but exactly when, would be difficult to predict. Some scientists claim that it would be possible, as the mechanism of fracture could be known better in terms of physics to identify precisely the measurable precursors theoretically (Matsu'ura. 1994). However, it would be tantamount to know exact details of every necessary factor including the stress state, distributions of weakness and strength of the earth's crust with their time variations etc. It would be practically impossible, at least at present.

Now, some others have this opinion that there are definite precursory phenomena if the earthquake process is looked from broader points of view, not just the traditional

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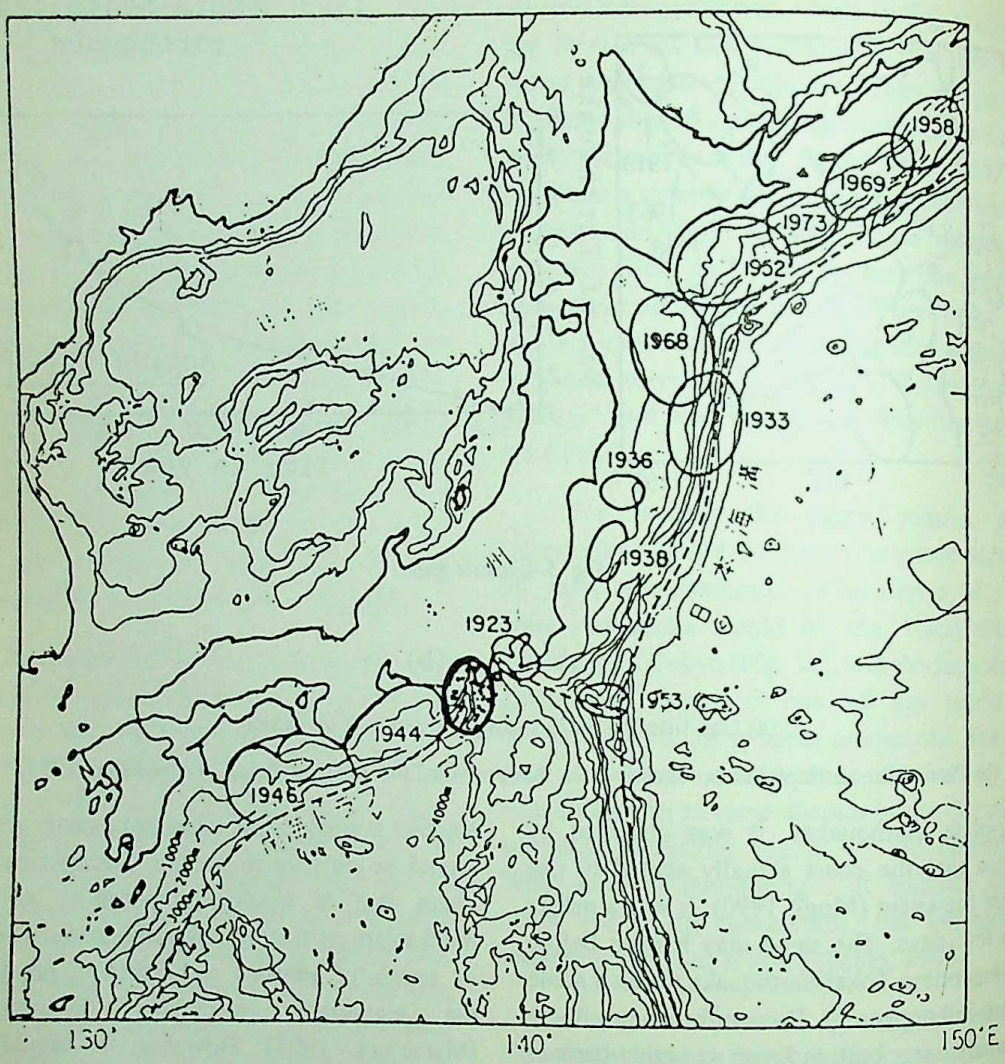

Fig. 5(c)–Gap (dotted oval) expected to be filled by "Tokai" Earthquake, but when ? Source Areas of M > 7.7 Shallow Earthquakes.

mechanical one. Examples include electro-magnetic field changes, large scale land deformations observable only by using satelite geodesy, such as GPS (Global Positioning System), radon and helium emission from the earth, level and temperature changes of underground water, and even abnormal behaviours of animals. This may be likened to looking at a wide variety of socio-political changes to forecast the stock- market. These suggested precursors, in particular the abnormal animal behaviors, have never been

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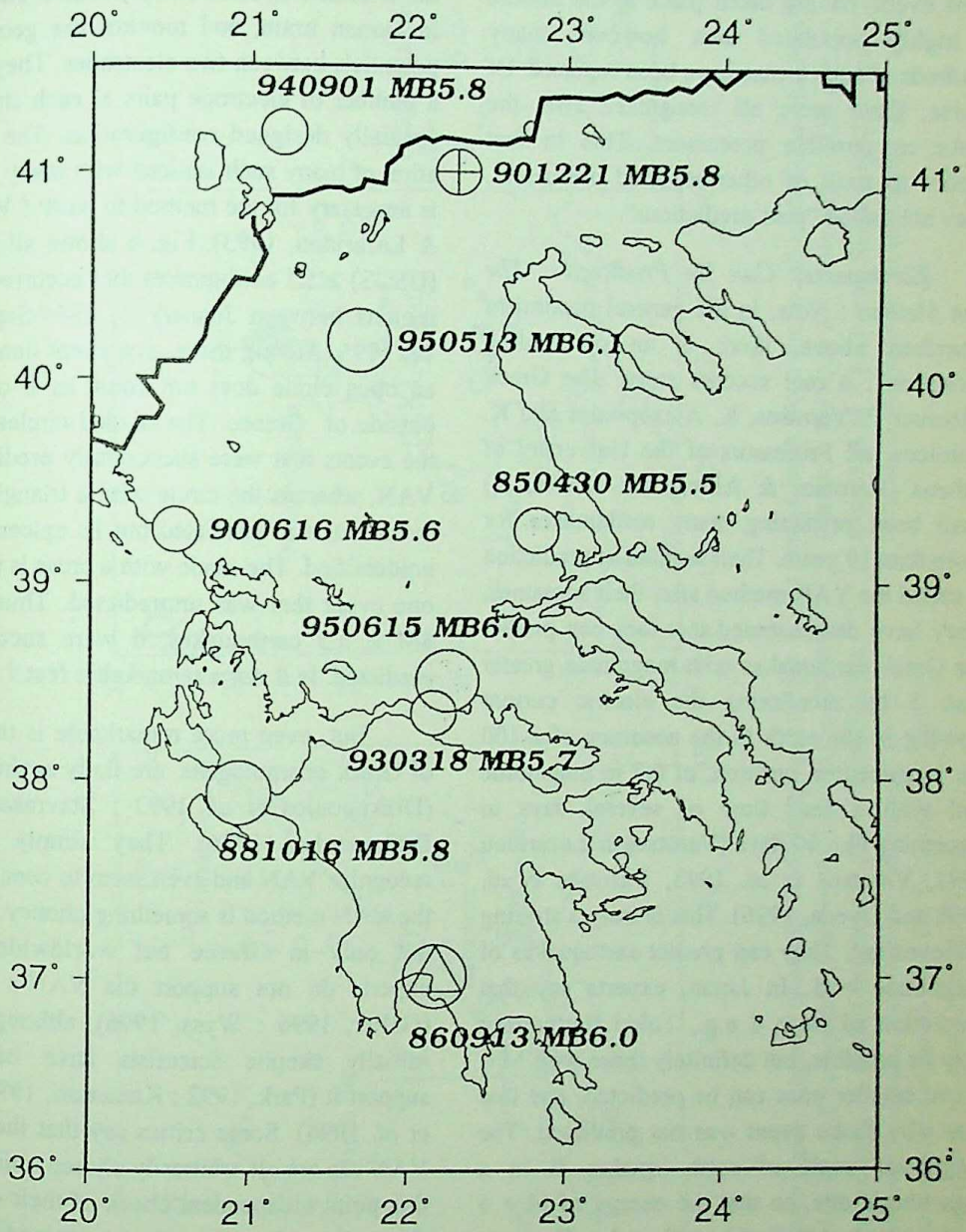

Fig. 6–All the earthquake M > 5.5 in Greek region for Jan. 1, 1984-Sept. 10, 1995.
6 events out of 8 have been predicted successfully.
For symbols, see text (after Al Damegh & Uyeda, to be published).

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considered to belong to the realm of science. Kobe event, having taken place in the middle of highly populated area, however, many hundreds of such a case have been reported. Of course, these were all recognized after the quake as possible precursors. This in fact applies to most of other reported precursors. They are called "post predictions".

Earthquakes Can Be Predicted : The Van Method : Now, in the general pessimism described above, there is an outstanding exception : a real success story. The Greek scientists P. Varotsos, K. Alexopoulos and K. Nomicos, all Professors of the University of Athens (Varotsos & Alexopouls, 1984a, b,) have been predicting many earthquakes for more than 10 years. Their method of prediction is called the VAN method after their surnames. They have demonstrated that they can predict the Greek earthquakes with magnitude greater than 5 by monitoring the electric current flowing in the earth to the accuracy of a 100 km in epicentral position, of 0.7 in magnitude and with a lead time of several days to something like 40 days (Varotsos & Lazaridou 1991, Varotsos *et al.* 1993, Varotsos *et al.* 1996 and Uyeda, 1996). This is truly a striking achievement. They can predict earthquakes of magnitude > 5. In Japan, experts say that prediction of M ≥ 8 e.g., Tokai Earthquake may be possible, but definitely those with M = 7 and smaller ones can be predicted, and that was why Kobe event was not predicted. The magnitude scale of earth- quakes is in a logarithmic one, so that the energy of M = 5 quake is only 1/900 of M = 7 quake. They can predict such small earthquakes.

The principle of their method is rather simple. They put electrodes in the earth, like the scientists of brain study put their electrodes in human brain, and monitor the geoelectric potentials between two electrodes. They install a number of electrode pairs at each station in specially designed configuration. The installation of many such stations with many dipoles is necessary for the method to work (Varotsos & Lazaridou, 1993). Fig. 6 shows all the Mb (USGS) ≥ 5.5 earthquakes that occurred in the regions between January 1, 1984-September 10, 1995. Among these, one event denoted by an open circle does not count as it occurred outside of Greece. The shaded circles denote the events that were successfully predicted by VAN, whereas the circle with a triangle is the event that was predicted but its epicenter was unidentified. The circle with a cross is the only one event that was unpredicted. Thus out of 8M ≥ 5.5 earthquakes, 6 were successfully predicted. Is it not a remarkable feat ?

But, even more remarkable is that most of Greek seismologists, are flatly against VAN (Drakopoulos *et al.* 1993 : Stavrakakis and Drakopoulos, 1996). They simply do not recognize VAN and even seem to consider that the VAN method is something phoney. Indeed, not only in Greece but worldwide, many experts do not support the VAN's success (Geller, 1996 : Wyss, 1996), although some initially skeptic scientists have begun to support it (Park, 1992 : Kanamori, 1996 : Park *et al.* 1996). Some critics say that the signals VAN see are all arbitrarily chosen noise. As to this point independent check of their originals data was made and it was ascertained that it is unlikely that they are noise (Nagao *et al.*, 1996a). Others say that VAN's success is simply by chance, that is to say, since many

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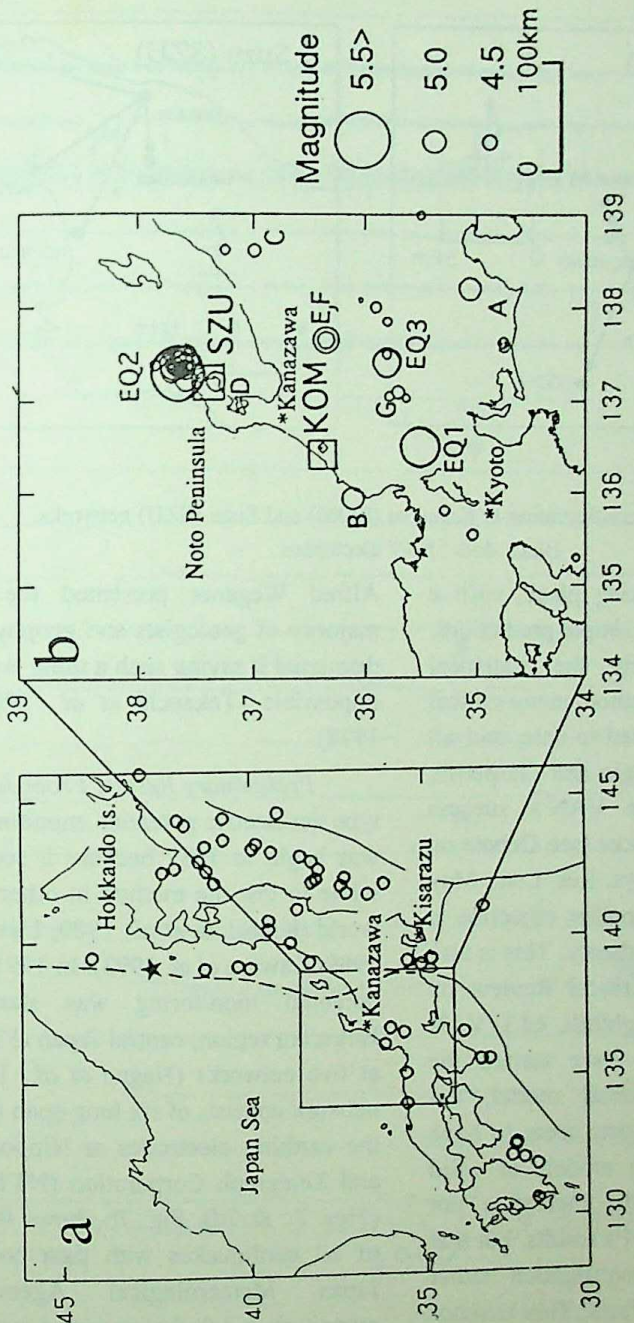

Fig. 7 (a)–Japanese region. Regional seismicity is shown by open circles representing M ≥ 7.0 earthquakes (1885-1988). Lines in the offshore area : plate boundaries. Dashed line through eastern Japan Sea is a newly proposed subducting plate boundary (Nakamura, 1986). Black star : epicenter of the M = 7.8 Off Southwest Hokkaido Earthquake of July 12, 1993. Asterisks : cities.

(b) Central Japan. Open circles : all earthquakes with JMA ≥ 4 (March 1, 1991-July 31, 1994). EQ 1, EQ2, and EQ 3 : three JMA M > 5.0 events. Rectangles KOM and SZU : areas in (c) and (d). A-G : events with 5.0 ≥ M ≥ 4.5.

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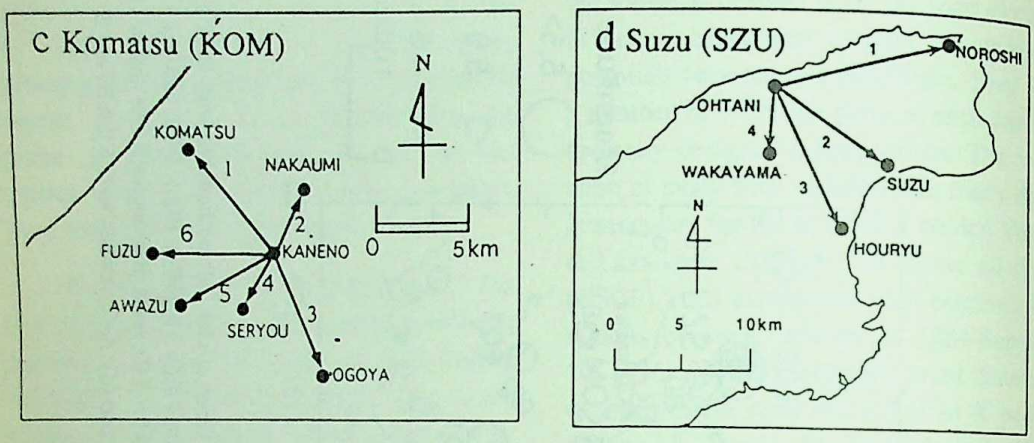

Fig. 7(c) and Fig. 7(d) Dipole configuration at Komatsu (KOM) and Suzu (SZU) networks. Black dots : NTT electrodes.

earthquakes have been taking place, such a success can be achieved by simple predictions. As to this point, namely the statistical significance of the VAN method, many critical reviews have been conducted to-date, and all but a few of them (Mulargia and Gasperini, 1992) concluded that the VAN's success cannot be attributed to chances (see Debate on VAN, Special Issue, Geophys. Res. Lett., May 27, 1996, R. Geller, ed.) Another objection is that the VAN method lacks theory. This is also hardly the case (see A Critical Review on VAN, 1996, Sir. James Lighthill, ed.). VAN scientists being physicists have started the work based on a theoretical model, but unfortunately the seismologists seem to have difficulty in understanding models of solid state physics. Certainly, the theory is not complete in explaining VAN's results, but that should encourage more investigation rather than dismiss the observed facts. This reminds the case of the continental drift theory. When Alfred Wegener presented the hypothesis, majority of geologists and geophysicists flatly dismissed it saying such a thing is theoretically impossible (Takeuchi *et al.*, 1964 : Uyeda, 1978).

Preliminary Results From Japan : VAN-type geoelectric potential monitoring in Japan was begin in 1987 because it seemed worth-while to test the method in other parts of the world (Kinoshita *et al.*, 1989; Uyeshima *et al.*, 1989; Kawase *et al.* 1993). In 1991, geoelectric potential monitoring was started in the Hokuriku region, central Japan (Figs. 7a & 7b) at two networks (Nagao *et al.*, 1996b). Each network consists of six long-span dipoles using the earthing electrodes at Nippon Telephone and Telegraph Corporation (NTT) exchanges (Figs. 7c & 7d). Fig. 7b shows the epicenters of all earthquakes with data collected from Japan Meteorological Agency (JMA), magnitude ≥ 4.0, that occurred in central Japan from March 1, 1991 to July 31, 1993. There

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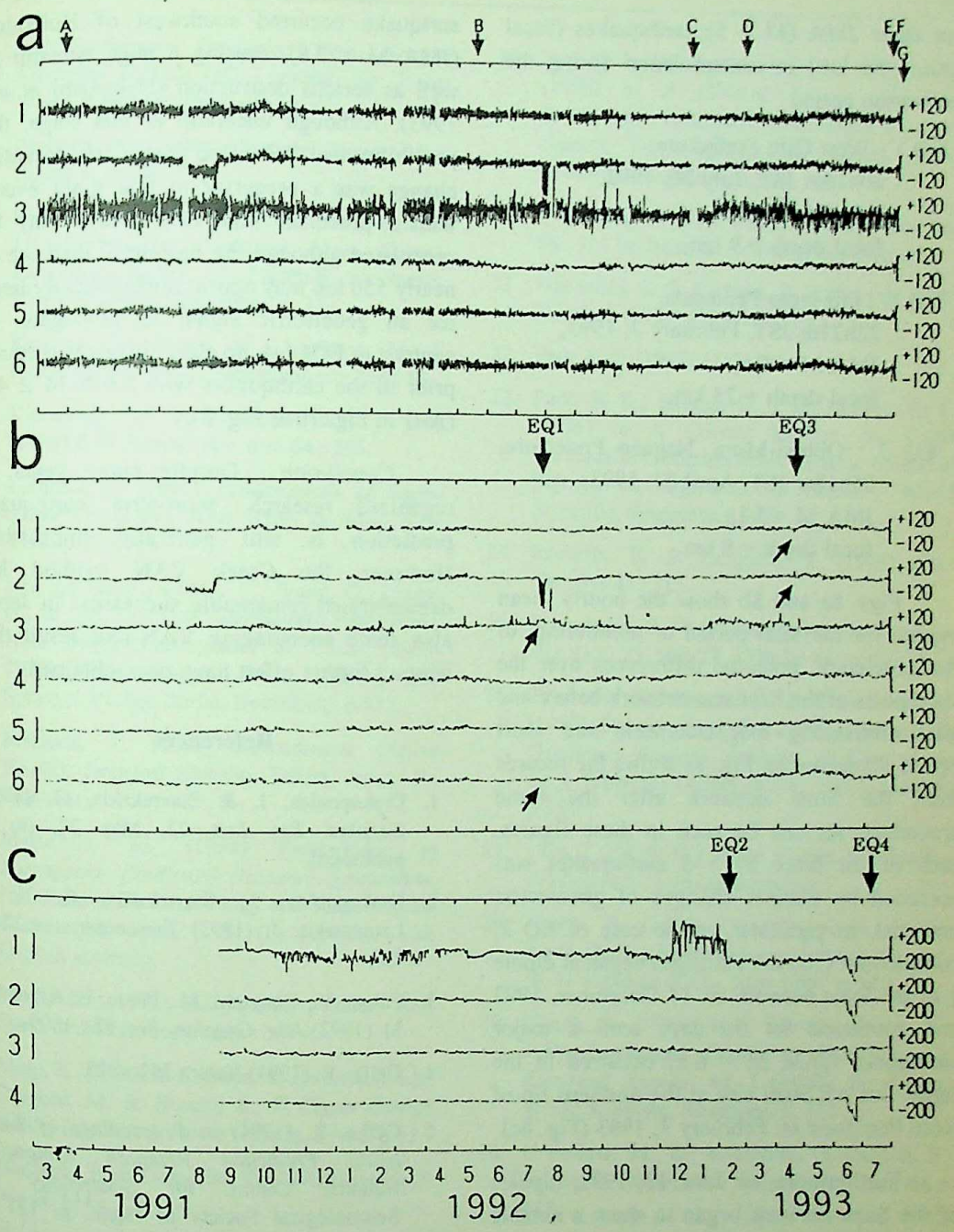

Fig. 8–Continuous records of hourly mean values of geoelectric potential differences of dipoles at Komatsu : (a) raw data and (b) : after cleaning . (c)–(after cleaning) networks : EQ 1-EQ 4 are indicated by arrows. Numbers : dipole numbers in Figs. 7c and 7d. Top arrows A-G : occurrence times of $5.0 \geq M \geq 4.5$ events.

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were three JMA (M > 5) earthquakes (focal depth < 50 km) in central Japan during the observation period :

EQ 1 : West Gifu Prefecture,
20h16m JST, July 30, 1992,
JMA M = 5.3,
focal depth = 9 km,

EQ. 2 : Off Noto Peninsula,
22h27m JST, February 7, 1993,
JMA M = 6.6,
focal depth = 25 km,

EQ 3 : Ohtaki-Mura, Nagano Prelecture,
05h18m JST, April 23, 1993,
JMA M = 5.1,
focal depth = 8 km.

Figs. 8a and 8b show the hourly mean values, for the total period of monitoring, of the geoelectric potential differences over the six dipoles of the Komatsu network before and after eliminating magnetotelluric and short period disturbances. Fig. 8c shows the records from the Suzu network after the same procedure. As can be seen in these figures, each of the three M > 5 earthquakes was preceded by distinct changes of geoelectric potential. In particular, in the case of EQ 2, conspicuous (500 mV) changes began at dipole 1 of the Suzu network on 14 December, 1992 and continued for 56 days until a major earthquake (JAM M = 6.6) occurred in the Japan Sea off Suzu city at the northern tip of Noto Peninsula on February 7, 1993 (Fig. 8c).

Furthermore, on June 13, 1993, dipoles of the Suzu network began to show a notable change in the geoelectric potential. The change ended on June 25. On July 12, a devastating eartquake occurred southwest of Hokkaido (JMA M = 7.8), causing a huge tsunami as well as serious destruction (Nakanishi *et al.*, 1993). Although uncertain at this stage, the possibility that, measured geoelectric potential change was a precursor to that giant event, with a precursor time of 27 days may be speculated although the epicentral distance of nearly 550 km may appear unrealistically large for an geoelectric signal to propagate. In contrast to EQs 1-4, no clear signals was found prior to the earthquakes with $5.0 \geq M \geq 4.5$ (A-G in Fig. 7b & Fig. 8).

Conclusion : Despite many years of organized research, short-term earthquake prediction is still generally impossible. However, the Greek VAN method has demonstrated remarkable successes. In Japan also some encouraging VAN-like result that warrant further effort have been obtained.

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SCIENCE LETTERS

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A phosphonate for management of betelvine *Phytophthora*

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Received November 23, 1996; Revised October 21, 1997.

Abstract *Piper betle* L. suffers heavy losses due to infection of *Phytophthora palmivora* (E) Butler, which causes leaf and foot rot. Spray and drenching (4 ml/l) of potassium salt of phosphonic acid at monthly interval could check the dieases efficiently. Since potassium phosphonate, does not have any residual problem or toxic effects, it's use will prove an asset for the crop.

(**Keywords** : potassium phosphonate / *Piper betle* / *Phytophthora palmivora*)

Betelvine (*Piper betle* L.) suffers from major crop losses due to foot and leaf rot infection caused by *Phytophthora palmivora* (E) Butler. The losses are sometimes so high[1] (80- 100%) that the gowers give up the cultivation[2]. A number of trials on management of this particular diseasc[3,4] has been conducted. With a view to choose a safer chemical for the management of present investigation has been conducted by repeated field trials for three years and the results are presented here in.

Mahoba Desawari cultivar a prized variety of betelvine was selected for these trials. The experiment was laid down in RBD (Randomized block design) in the beds of 1.0 m × 0.3 m having approximately 100 vines, 10 vines were randomly tagged for recording the observations. The experiment was conducted in three replication. Spray of the test chemicals as mentioned hereunder was made at monthly intervals.

Aliette, a known oomycetes management chemical (fosetyl alumunium) alumunium - tris-e-ethyl phosphosphonate was also used as a positive control. Observations on leaf rot intensity and vine mortality due to foot rot were conducted at monthly intervals for three cropping seasons. The results are presented in terms of percentage disease control and disease intensity. The experimental spray was done from July to October whereas the observations were recorded upto December.

Table 1 & 2 show that spraying and drenching with 4 ml/l of Potassium phosphonate (T-2) at monthly interval could manage the disease to almost 70% or more in all the years.

Coffey and Fenn[5] demonstrated *in vitro* efficacy of phosphorus acid along with aliette

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Table 1 – Leaf rot intensity management by different chemicals.

Experiment	Chemicals	% Disease management		
		1992	1993	1994
T-1.	Pot. phosphonate (4ml/l Soil drench)	61(19)	76(11)	70(16)
T-2.	Pot. phosphonate (4ml/l Soil drench) + Spray	73(13)	79(10)	76(13)
T-3.	Pot. phosphonate (4ml/l) + Captaf 6g/l drench	56(21)	50(21)	52(23)
T-4.	Aliette 3gm/l Spray only	51(25)	50(21)	51(23)
T-5.	Control (Water spray)	(51)	(42)	(47)

Figures in brackets are the nearest score of leaf spot (average of 3 replications).

Table 2 – Vine mortality management due to foot rot infection.

Experiment	Chemicals	% Disease management		
		1992	1993	1994
T-1.	Pot. phosphonate (4ml/l Soil drench)	70(6)	72(4)	72(5)
T-2.	Pot. phosphonate (4ml/l Soil drench) + Spray	80(4)	77(4)	73(5)
T-3.	Phot. phosphonate (4ml/l) + Captaf 6g/l drench	66(7)	53(7)	60(7)
T-4.	Aliette 3gm/l Spray only	70(6)	61(6)	61(7)
T-5.	Control (Water spray)	(20)	(15)	(18)

Figures in brackets are the nearest score of mortality 3 replications.

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and fosetyl AL against seven of the eight *Phytophthora* isolates tested. The compound was quite effective against *P. capsicii* at 180 ug/ml *in vivo*[6] and the results were comparable with fosetyl AL and metalaxyl, the systemic fungicides.

Quimette and Coffey[7] demonstrated the efficacy of related phosphonates (monoethyl, diethyl and dimethyl) and a potassium salt (potassium phosphonate) against 34 *Phytophthora* isolates belonging to 9 species. The chemical may be considered for the management of betelvine *Phytophtora* disease.

Authors wish to express their sincere gratitude to the Dr. P.V. Sane, Director, N.B.R.I., Lucknow for his constant encouragement. Help rendered by Sri P.R. Yadav, T.A. for laying out the trial, experimental observation etc. is gratefully acknowledged. M/s Rallis India supplied the test chemicals for these experiments.

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Effect of pyridoxine on proteases in germinating chickpea

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Abstract Chickpea (*Cicer arietinum* L; genotypes : H 88 - 237 and H 86 - 96) seeds were germinated at 25±2°C in a BOD incubator. At two days interval and upto eight days, the cotyledons and embryonic axes were separated, and were analyzed for acid and neutral protease activities. Both the activities increased with progress of germination in both the organs and in both the genotypes. Soaking of seeds in 0.01% pyridoxine hydrochloride solution for 14 h before germination, further enhanced the protease activities, compared with untreated controls.

(**Keywords** : pyridoxine / proteases / germination / chickpea)

Dry seeds contain very little free amino acids[1], although, these contain several different proteases[2]. Both neutral and acid proteases have been indentified in quiescent legume seeds[3,4]. Proteases hydrolyze storage proteins in protein bodies of living cotyledons in dicotylednous seeds, to supply amino acids for protein synthesis in growing axis[1]. Protease activity (both neutral and acid) increases during seed germination[5].

Vitamins of B-complex group also increase during seed germination and deficiency of vitamin B_6 disturbs the amino acid metabolism. On the other hand, addition of vitamin B_6 has favourable effect on seed germination[6]. Pyridoxine (vitamin B_6) is a precursor for synthesis of pyridoxal phosphate, a coenzyme important in amino acid metabolism. Although, pyridoxal phosphate is not directly associated with proteases, pyridoxine increases protein mobilization in germinating triticale seeds[7]. The favourable effect of pyridoxine on neutral and acid proteases in germinating chickpea is reported here.

The proteases were extracted and assayed according to Rao and Croy[8]. Extraction was carried out at 0-4°C by homogenization with phosphate buffer (0.05M; pH 7.5) containing 0.01M cysteine and 35 mM EDTA. Acid protease activity was assayed by incubation of the extract using 1% bovine serum albumin and citrate buffer (0.2M; pH 5.0) at 40°C. Neutral protease activity was assayed by incubation with 1% casein prepared in phosphate buffer (0.2 M; pH 7.0). The released amino acids were assayed by ninhydrin method. Protease activity was expressed in terms of leucine released.

The results obtained are depicted in Fig 1. Both the neutral and acid protease activities increased with progress of germination, in cotyledons as well as in embryonic axis in both the genotypes as well as in treated and untreated seedlings. This indicates that these proteases participate in protein degradation in

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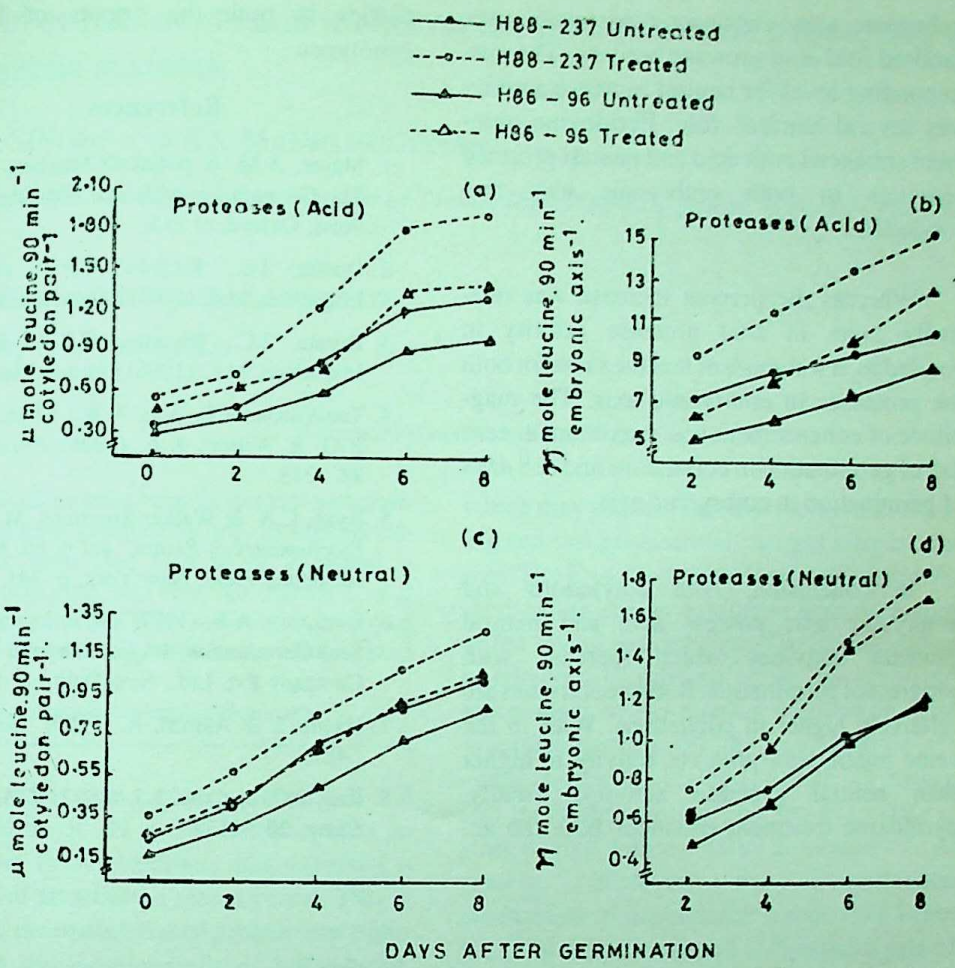

Fig. 1 – Acid protease (a and b) and neutal protease (c and d) activities per cotyledon pair (a and c) and per embryonic axis (b and d) in chickpea (genotypes : H 88-237 and H 86-96) seedlings raised from untreated and pyridoxine - treated seeds. (The plotted values are means of four replicates).

cotyledons and in turnover of protein in embryonic axis. Whereas, neutral protease activity is understandably associated with protein degradation in cotyledons, the role of acid protease has been implicated in intracellular metabolism[5]. Analysis of data presented in Fig. 1 reveals that compared with neutral protease activity, acid protease activity is several fold higher in embryonic axis, whereas in cotyledons, it is less than two fold. This is consistent with the preferred role of acid protease in protein turnover in the vacuoles of growing tissues. Despite much higher weight of cotyledon than that of embryonic axis, the role of acid protease in senescing cotyledons should not be under estimated. Compared with

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embryonic axis, cotyledons possessed over hundred fold acid protease activity. The corresponding level for neutral protease activity was several hundred fold. Pyridoxine treatment enhanced both acid and neutral protease activities in both embryonic axis and cotyledon.

Whereas the percent increase was relatively more in acid protease activity in cotyledon, it was more or less the same for both the proteases in embryonic axis. The magnitude of enhancement was maximum at zero day of germination in cotyledons and at 8 days of germination in embryonic axis.

In conclusion, both cotyledons and embryonic axis possess acid and neutral protease activities which increase with progress of germination. Both the activities are relatively higher in cotyledons. With in the same organ, acid protease activity is higher than neutral protease activity. Finally, pyridoxine treatment enhances both the activities in both the organs of both the genotypes.

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Effect of substituents and media on the photochromic properties of azobenzene systems

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Abstract *E*-azobenzene bearing electron-withdrawing and ionizable substituents (e.g. 2) exhibits solvatochromic behaviour, high % of *Z* isomer at photostationary state, and very fast thermal $Z \rightarrow E$ isomerization in protic polar solvents. A rotational mechanism has been suggested for the isomerization process.
(**Keywords** : photochromism/azobenzene)

The reversible photoinduced *E, Z* isomerization of -N = N- chromophore in azobenzene (1) compounds has attracted a great deal of attention in recent years[1]. This is because of the usefulness of azobenzene compounds in the development of information storage assemblies, chemical and biochemical sensors, artifical vision, photocontrol of micellar and enzymatic reactions, and many other applications in molecular electronics[2-4]. Naturally, understanding the mechanism of photoinduced *E, Z* and also thermal *Z, E* isomerization of such chromophores is of utmost importance and it has become the subject of multi-disciplinary concern[1].

The azobenzene type molecules are characterized by a large (π,π^*) - $(n\text{-}\pi^*)$ state gap, which may cause restricted intersystem crossing and fast geometrical changes after excitation. The $E \rightarrow Z$ isomerization yields are lower on the high energy excitation than excitation of the lowest excited state. The isomerization is believed to proceed either *via* inversion mechanism or *via* rotation mechanism. The inversion mechanism in the ground and $^1(n\text{-}\pi^*)$ - state is widely accepted and there is a feeling that the deactivation of the $^1(\pi, \pi^*)$ - state at least begins with a rotational motion[1,3,5]. At present, however, the isomerization mechanism of azobenzene compounds is not yet fully understood and it consitutes one of the most interesting issues of azobenzene spectroscopy and photochemistry.

It is believed that azobenzene compounds with electron push-pull character undergo a rotation pathway involving a dipolar transition state. Further a rotation mechanism is characterized by large solvent effect on thermal $Z \rightarrow E$ isomerization[1]. Herein we describe the relative importance of electron donating and particularly electron attracting substituents in controlling the isomerization process of

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azobenzene by studying the isomerization of 4-(p- carboxyphenylazo)-2-(methylene octadecanoate)-phenyl octadecanoate (2) bearing electron withdrawing groups and demonstrate that such electron pull-pull azobenzene compounds exhibit isomerization *via* rotational pathway.

Compound 2 was synthesised as outlined in Scheme 1. 2 : 63% yield; m.p. 92 - 93° C; CHN ($C_{48}H_{80}N_2O_6$) ; calculated, C, 73.84, H, 10.25, N, 3.50; found : C, 74.40%, H, 9.97, N, 3.45; uv-vis; λ_{max}, nm (solvent, ε) : 361 (MeOH, 27302), 348 (n-heptane, 24653), 352 (chloroform, 26738), 361 (acetonitrile, 25357); IR (KBr) ; 2921, 2854, 1683, 1104, 1073 cm^{-1}; ^{1}HNMR (300 MHz, $CDCl_3$) δ: 0.82 (t, 6H, $-CH_3$), 1.22 (s, 54H), 2.60 (t, 2H, $-OCOCH_2$, 5.10 (s, 2H, Ar-CH_2-), 7.10 (s, 1H, Ar-H), 7.90 - 8.00 (m, 4H, Ar-H), 8.20 - 8.30 (m, 2H, Ar- H).

As compared to parent azobenzene (1, 313 nm), the π,π* absorption band of compound 2, which is shifted to longer wavelength by *ca.* 48 nm in methanol, showed red-shifted absorption as the solvent polarity was increased. Irradiation of 2 (Fig. 1) at its π, π* λ_{max} in organic solvents gave a photomixture rich in *Z* isomer. Thus the photomixture consisted of *E* and *Z* forms of 2 with per cent composition at photostationary state (PSS) as follows : in benzene, *E* + 18.6, *Z*= 81.4 ; in chloroform, *E* = 27.8, *Z* = 72.0. In protic polar solvents like methanol, the PSS could not be determined owing to extremely fast back thermal isomerization.

Under thermal conditions, 2 was found to undergo $Z \rightarrow E$ isomerization with first order rate kinetics as in the case of parent azobenzene. The rates of thermal $Z \rightarrow E$ isomerization in different solvents are as follows : ($\times 10^{-3}$ s^{-1}) *n*-heptane : 2.40, benzene : 1.11, chloroform : 2.75, acetonitrile : 15.40.

Thus, compound 2 in methanol not only showed bathochromic shift in its absorption band but also underwent very fast $Z \rightarrow E$ thermal isomerization. Such dependence of rates of thermal isomerization is expected in azobenzene systems bearing strong electron-donating and electron- accepting substituents at o or p- positions of the aryl ring. Involvement of hydrazo tautomer for the fast thermal $Z \rightarrow E$ isomerization of p-N,N dimethylamino substituted azobenzene systems have been proposed[8,9], but such processes are not possible in 2 because it lacks strongly conjugating electron donating groups. To further understand the isomerization process, we have studied the $Z \rightarrow E$ isomerization of 2 in acetonitrile containing methanol. It has been found that presence of methanol in acetonitrile causes rapid increase in the thermal isomerization of 2 (rate of $Z \rightarrow E$ in 5 % methanol acetonitrile is 32×10^{-2} s^{-1}).

These results of the absorption spectra and isomerization of 2 can be understood in terms of the rotational mechanism of isomerization as depicted in Scheme 2. In polar solvents, the carboxylic group completely dissociates and the proton is taken up by the basic azo (-N=N-) group resulting in its partial protonation, and a negatively charged carboxyl group. This could stabilize the highly polar rotational transition state involved in the isomerization process. Thus, the nature of substituents and the surrounding media are of crucial significance in controlling the dynamics of the

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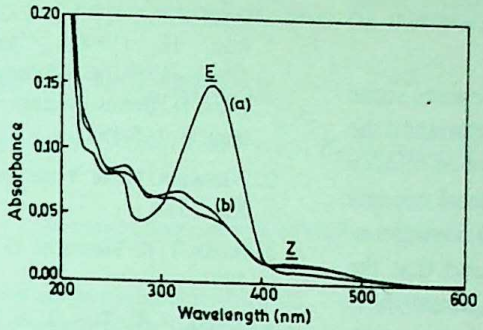
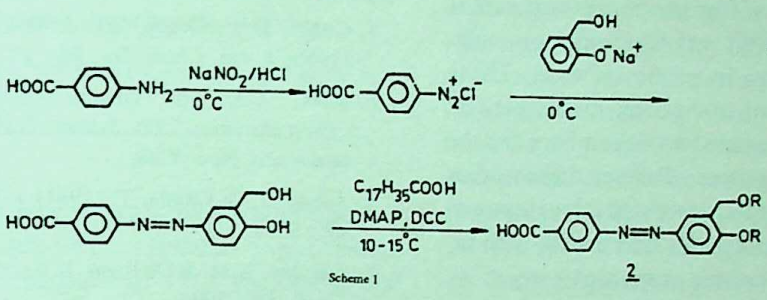
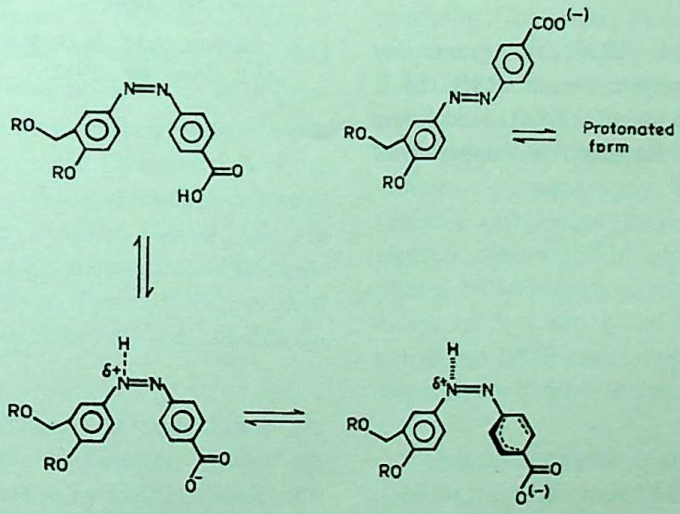


Fig. 1



Scheme 1



Scheme 2 R.T.S

Fig. 1 – Uv-vis absorption spectra of 2 in chloroform, (a) before irradiation, (b) after irradiation.

Scheme 1 – Synthetic route of 2.

Scheme 2 – Mechanism of isomerization of 2 in protic polar solvents *via* rotational transition state.

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isomerization process of azobenzene compounds.

Thus, this communication presents some novel observations which help understand the rotational aspecs of the mechanism of -N=N= isomerization. Besides the structural novelty of newly prepared chromophore 2 having amphilic character, it has been found that the ionizable carboxylic groups can direct these chromophores to undergo isomerization by rotational process. Chromophore such as 2 is also found to exhibit very fast back isomerization (cis to trans) in protic solvents. These studies have a lot of bearing in the general context of azobenzene photochemistry and the thermal reversal process. Further, these studies provide new directions towards development of azobenzene molecular framework with interesting photochromic properties.

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Efficient method for deamination of amino pyrimidines

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Received September 9, 1997; Revised February 19, 1998.

Abstract Deamination of amino pyrimidines has been carried out by using isopentylnitrite in anhydrous dimethylformamide at 65- 70°C. This is a rapid procedure for deamination of heteroaryl amines.

(**Keywords** : IR/^{1}HNMR.deamination/amino pyrimidines/isopentylnitrite)

In the recent years much attention has been focussed on the synthesis of pyrimidine derivatives because of their biological and medicinal importance[1-4]. They form the important constituents of nucleic acids and vitamin B_1^5. Cytosine nucleosides have been proved to be the most effective therapeutic agents for the acquired immune deficiency syndrome (AIDS)[6]. Most recently, it has been proved· that the cytosine derivatives are capable in binding in a sequence specific manner to DNA and RNA[7]. Pyrimidines also form a constituent of liquid crystal compositions[8].

There are many methods used for deamination of arylamines, however, deamination of amino pyrimidines under anhydrous condition using isopentylnitrite in DMF has many advantages over the other methods because of simple workup, mild reaction conditions, better yields, no side reactions observed as in dioxane solvent and the product can be isolated by evaporation of the solvent.

The starting material ethyl 2-benzoyl-3-dimethylaminorpopenoate **1** was prepared by reacting ethyl benzoylacetate with N,N-dimethylformamide dimethylacteal in methanol by reported method[9], followed by its reaction with guanidine sulphate in methanol to form ethyl 2-benzoyl-3-guanidino propenoate **2**. The formation of compound **2** was ascertained by the appearance of –NH band at 3350- 3100 in IR spectrum and absence of 2-dimethylamino group in its ^{1}H NMR spectrum. Compound **2** on cyclisation in the presence of sodium ethoxide in ethanol gave a mixture of 2-amino-4-hydroxy-5- benzoyl pyrimidine **3** and 2-amino-4-phenyl-5-carbethoxypyrimidine **4** which were separated by column chromatography. Similary, cyclisation of **2** with sodium methoxide in methanol yielded transesterified product 2-amino-4-phenyl-5-carbmethoxypyrimidine **5**. Deamination of **3, 4** and **5** and isopentylnitrite in anhydrous DMF gave oxo-products **6,7** and **8** respectively in 50-6-% yields.

Unless stated otherwise all the chemicals used were of AR grade and used without further purification. Anhydrous dimethylformamide was used after double distillation. Melting points were determijned on a Tottoli apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 421. ^{1}H NMR spectra were taken in DMSO-d_6 on a Varian

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200 gemini spectrometer with TMS as an internal standard.

The amino pyridimines used for deamination such as 2-amino-4- hydroxy-5-benzoyl pyrimidine **3**, 2-amino-4-phenyl-3- carbethoxypyrimidine **4** and 2-amino-4-phenyl-5-carbmethoxypyrimidine **5** were prepared by literature method[10].

Deamination of aminopyrimidines : Typical Procedure : In a 100 ml three necked flask fitted with a reflux condenser and dropping funnel, a solution of aminopyrimidine (10 mmol) in anhydrous dimethylformamide (5 ml) maintained at 65°C, to which a solution of isopentylnitrite (10 mmol) in anhydrous dimethylformamide (5 ml) was added over a period of 10 min. and the reaction mixture stirred further for 30 min. and concentrated. The separated solid was purified by column chromatography using silica gel and solvent system chloroform ; methanol (95:5, v/v) to furnish the desired product.

Physical, analytical and spectral data of the deaminated compounds have been incorporated in the Tables (1 and 2) respectively.

Table 1 – Physical and analytical data of deaminated compounds.

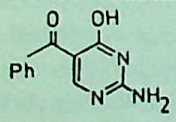
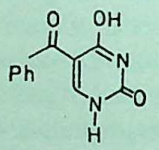
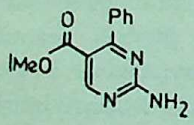
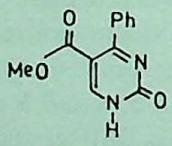
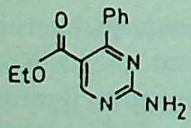
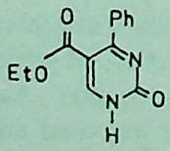
Sr. No.	Starting Compound	Deaminated product	m.p. (°C)	Yield (%)	Mol. formula	Elemental Analysis Found/calcd. (%) C	H	N
1	 (3)	 (6)	above 250	65	$C_{11}H_8N_2O_3$	61.03 61.13	3.65 3.70	12.94 12.95
2	 (5)	 (8)	215	45	$C_{12}H_{10}N_2O_3$	62.61 62.62	4.33 4.34	12.12 12.16
3	 (4)	 (7)	212	50	$C_{13}H_{12}N_2O_3$	63.91 63.95	4.90 4.91	11.41 11.46

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Table 2 – Spectral data of deaminated compounds.

Sr.No.	Deaminated Product	IR (Kbr) v (cm^{-1})	^{1}HNMR (DMSO-d_6) δ (ppm)
1.	Compd. No. **6**	3350-3200 (NH and OH), 1690 (> C=O), 1660 (> C=O) 1620 (C=N)	7.2–7.6(5H,m,Ar–H), 8.35 (1H,d,J=8Hz, =CH), 10.35 (1H,d, J=8Hz, NH), 10.6 (1H,s,OH).
2.	Compd. No. **8**	3450-3350(NH), 1740(ester > C=O), 1660 (>C=O), 1620 (C=N)	3.65(3H,s,–OCH_3),7.4–7.55 (H,m,Ar-H), 8.35(1H,d,J=8Hz,=CH), 10.5(1H,d,J=8Hz,NH).
3.	Compd. No. **7**	3400–3250(NH), 1750(ester>C=O), 1665 (>C=O), 1620 (C=N)	1.1(3H,t,J=8Hz,CH_3), 4.2 (2H,q,J=8Hz,OCH_3), 7.4- 7.55 (5H,m,Ar-H), 8.3 (1H,d, J=8Hz,=CH), 10.3 (1H,d, J=8Hz,NH).

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Twisted actions of cyclic groups

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Abstract We prove that if the cyclic group of order 3 acts freely on a topological space X, then the induced twisted action of the cyclic group Z_{3n} on the n-fold cartesian product X^n of X is free if and only if n is a power of 3.

(**Keywords** : cyclic group/twisted action)

Let X be a topological space and G be a topological group acting continuously on X (see Bredon[1] p. 32 for basic definitions). Then every element $g \in G$ can be thought of as a homeomorphism of X. We say that the action is *free* if each $g(\neq e)$ moves every point of X, i.e., for each $x \in X$, $g.x \neq x$. Existence and classification of free actions on various nice spaces has been extensively studied[1-6]. Determining free actions on the products of spheres and various other projective spaces (real or complex) has been an interesting problem. Various tools from homology and cohomology groups to spectral sequences have been successfully applied in such a study. A particular situation which occurs very frequently in the investigation of free actions on products of spaces is the following: Let a cyclic group Z_m, $(m \geq 2)$ act freely on a topological space X. This is equivalent to saying that there is a homeomorphism $h : X \to X$ of period m, which has the property that each of $h, h^2, \ldots, h^{m-1}$ moves every point of X. Consider the n-fold, $(n \geq 2)$ Cartesian product X^n of X. Then the homeomorphism h on X defines a map $T : X^n \to X^n$ given by the formula

$$T(x_1, x_2, \ldots, x_n) = (x_2, x_3, \ldots, x_n, h(x_1)) \quad (1)$$

Clearly $T^{m.n} = I_{X_n}$, which means T is indeed a homeomorphism of the product space X^n of period $m.n$. In other words, T generates an action of the cyclic group $Z_{m.n}$ on the product space X^n. An action of Z_{mn} on the product space X^n defined by the formula (1) is called a *twisted action* induced by the given action of Z_m on the space X.

Now the question is : If the given action of Z_m on X is free, when can we say that the twisted action of the cyclic group $Z_{m.n}$ on the product space X^n is also free? Cusick and Tennenbaum[7] have studied this question for the case $m = 2$. They have also given some interesting applications of this case. In this communication we answer the above question completely for the case $m = 3$. Our result is the following.

Theorem 1 : If Z_3 acts freely on a space X, then for each $n \geq 2$, the twisted action of the cyclic group Z_{3n} on the product space X^n is free iff n is a power of 3.

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For any homeomorphism $h : Y \to Y$, let Fix h denote the set of all fixed points of h, i.e. Fix $h = \{y \in Y \mid h(y) = y\}$. We have an easy

Lemma 1 : Let $h : Y \to Y$ be a homeomorphism of period $n \geq 2$, and for any m, $1 \leq m \leq n$, let $d = gcd(m,n)$. Then Fix h^d = Fix h^m.

Proof: Since m is a multiple of d, we have Fix $h^d \subseteq$ Fix h^m. Conversely, suppose $a \in$ Fix h^m. This means $h^m(a) = a = h^{-m}(a)$. We already know that $h^n(a) = a = h^{-n}(a)$. Let us write $d = m.r + n.s$, $s \in Z$. By changing the signs of m and n, we can assume that r and s are non-negative. Then

$$h^d = h^{m.r+n.s} = \underbrace{h^m \circ \ldots \circ h^m}_{r-times} \circ \underbrace{h^n \circ \ldots \circ h^n}_{s-times}$$

whence $h^d(a) = a$. Thus Fix $h^m \subseteq$ Fix h^d. □

By the statement that a homeomorphism acts freely on a space X, we mean that homeomorphism moves every point of X. Now we have

Lemma 2 : Let n be a multiple of an integer $r \geq 1$. If a homeomorphism h acts freely on X, then h^r acts freely on X^n.

Proof : Put $n = r.k$. We can write an element $x \in X$ as follows :

$$x = (\underbrace{a_1, \ldots, a_r}, \underbrace{a_{r+1}, \ldots, a_{2r}}, \ldots, \underbrace{a_{(k-1)r+1}, \ldots, a_{kr}}),$$

which expresses the n-tuple as a k-tuple of r-tuples of elements of X. Then, by definition,

$$h^r(x) = (\underbrace{a_{r+1}, \ldots, a_{2r}}, \ldots, \underbrace{a_{kr}, h(a_1), \ldots, h(a_r)}),$$

Now, h^r fixes x means

$$a_1 = a_{r+1} = \ldots = a_{(k-1)r+1} = h(a_1),$$

which is a contradiction, since h acts freely on X. Thus h^r cannot have a fixed point in X^n, and so the action is free. □

Proof of Theorem 1: Let $h : X \to X$ be a homeomorphism of X which generates the action of Z_3 on X. Consider the homoemorphism $T : X^n \to X^n$ defined by eqn. (1) using h, which generates the action of Z_{3n} on X_n. We must show that the latter action is free iff n is a power of 3.

First suppose that n is a power of 3. Let k be an integer, $1 \leq k < 3n$. We must show that T^k has no fixed points. By Lemma 2, T has no fixed points. Let $d = gcd(k, 3n)$. By Lemma 1, Fix T^k = Fix T^d. Since n is a power of 3, d is also a power of 3. Also, since $d < 3n$, d must divide n. Therefore, by Lemma 2, T^d has no fixed points. It follows that T^k has no fixed points $\forall\, k$, $1 \leq k$ $3n$, i.e., the action of Z_{3n} on X^n is free.

Conversely, suppose n is not a power of 3. Then we can write n as

$$n = 3^l(3m+1) \quad \text{or} \quad n = 3^l(3m+2),$$

where $l \geq 0$ and $m \neq 0$. In both of these cases, we will show that there is a power T^r of T, $r < n$ which has a fixed point in X^n. This will mean the action of Z_{3n} on X_n is not free.

Case 1 : Suppose $n = 3^l(3m+1)$. Note that $\forall a \in X$, the element

$$(a, (h(a), h^2(a), a), \ldots, (h(a), h^2(a), a))$$

where excepting for the first coordinate, all others have been grouped into m triples, represents a $(3m+1)$-tuple of X. If $l = 0$, then $n =$

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$(3m+1)$, and it is easily checked that the above point of X is fixed by T^3. If $l \geq 1$, then we will write an n-tuple $x \in X$ as

$$x = (b, (h(b), h^2(b), b), \ldots, (h(b), h^2(b), b)),$$

where $b = (a_1, a_2, \ldots, a_{3l})$ is a 3^l-tuple of elements of X; here $h(b)$ means $(h(a_1), \ldots, h(a_{3l}))$, etc. Now one can easily verify that the above element x is fixed by T^{3l+1}. In fact when we apply T^{3l+1} on x, the first 3^{l+1} elements viz. $(b, (h, b), h^2(b))$ are moved to the right extreme with h applied on each one of them, and then the result is the same point x. Evidently, $3^{l+1} < 3^l(3m+1) = n$.

Case 2 : Next, let $n = 3^l(3m+2)$. Again the explanation is analogous. For any $a \in X$, $(a, h^2(a), (h(a), a, h^2(a)), \ldots, (h(a), a, h^2(a))$ is evidently $(3m+2)$- tuple of elements of X. If $l = 0$ then $n = 3m+2$ and one checks easily that the above point of X^n is fixed under the map T^3. If $l \geq 1$, we can write an n-tuple of elements of X as

$$x = (b, h^2(b), (h(b), b, h^2(b)), \ldots, (h(b), b, h^2(b)))$$

where $b = (a_1, a_2, \ldots, a_{3l})$ is a 3^l-tuple of elements of X. Once again, if we apply the map T^{3l+1} on the above element x we find that x is a fixed point. As before, the first three coordinates of x which account for first 3^{l+1}-tuple of x are moved to the extreme right with h applied on each coordinate. The result is evidently the same point x. Also, $3^{l+1} < 3^l(3m+2) = n$ is evidently true.

Remark 1 : We do not know if a result similar to the main theorem is also true for each cyclic group Z_m, $m \geq 4$.

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Effect of ablation of preputial gland on stud male - induced protection of implantation in food - deprived mice

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Abstract There was no significant difference in food-deprived females in protecting implantation when housed either with intact or preputialectomized stud males. In both cases most of the females became pregnant. Findings suggest that ablation of preputial gland did not prevent stud male protection on implantation in food deprived females.

(**Keywords :** preputial gland/ stud male / implantation failure/ food-deprivation/mice)

It is well established that food deprivation during the preimplantation period induces implantation failure in mice[1–3]. The presence of stud male effectively prevents implantation failure in food deprived females[4]. A strong circumstantial evidence suggests that the stud male-originating protective stimulus is pheromonal and acts on females through main olfactory pathways[5,6]. Preputial glands of male rodents have long been suspected as sites of pheromone production. In mice, existing evidence indicates that the pheromone(s) involved in sexattraction[7] are localized in male preputial gland. Likewise, the female preputial glands are important in the development of social behaviour in mice[8]. Since the preputial glands take part in many pheromonal influences, its involvement in control of stud male pheromone production is suspected. Hence, the present investigation was designed to evaluate the involvement of preputial glands on the production of stud male pheromone involved in the protective effect on pregnancy.

All females and stud males belonged to the Swiss strain. Virgin females, 10-12 weeks old and wieghing 25-30g were monogamously paired with intact or preputialectomized stud males. On finding the vaginal plug (day 1 *post-coitum*), the females were separated from the stud males. They were divided into four groups, housed individually in cages (26 × 18 × 14 cm) and treated as follows : *Group I* : Deprived of food for 48h (from 10 h on day 4 to 10 h on day 6 *post-coitum*) and housed with preputialectomized stud males. *Group II* : Deprived of food for 48h as in group I and housed with intact stud males. *Group III* : Deprived of food for 48h as in groups I and II and housed without any male. *Group IV* : Controls : Left undisturbed after separation from stud males.

Soon after the termination of fasting, food was made available *ad libitum* to the females. The stud male (group I and II) was confined in an expanded metal corral, 15 X 12 X 9 cm and placed in the cage housing the females. Preputial glands were removed from the experienced stud male as per the procedure[9] and were used for mating after 30 days following

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Table 1– Effect of ablation of preputial gland on stud male- induced protection of implantation in food-deprived females.

Group and Treatment	Proportion and % of Females		
	With Implantation Failure*	Becoming Pregnant	Becoming Pseudopregnant
I. Food deprivation + Preputialectomized stud male	3/16 (18.75)	12/16 (75.0)	1/16 (6.25)
II. Food deprivation + Intact stud male	3/14 (21.43)	11/14 (78.57)	0/14 ---
III. Food deprivation	9/12 (75.00)	3/12 (25.00)	0/12 ---
IV. Normally fed and left undisturbed	0/12 ---	11/12 (91.67)	1/12 (8.33)

*Significance of differences : I Vs II, N.S.
I Vs IV, N.S.
I Vs III $p < 0.001$
II VS III $p < 0.001$

surgery. Vaginal smears were examined daily from all females upto day 11 *post-coitum* and the presence of cornified cells was taken as an indication of the implantation failure[3] Females were failed to show vaginal cornification were killed on day 11 *post- coitum* to confirm pregnancy. Females which could not exhibit vaginal cornification and without implantations were presumed to be pseudopregnant. The data were analysed by the X^2 test.

Results are presented in the Table 1. Food-deprived females housed with preputialectomized stud males exhibited a significant reduction (Group I) in implantation failure comparable to that seen in food-deprived females housed with intact stud males. Most of the females became pregnant. Females housed without any males exhibited a high rate of implantation failure. Females which were mated with preputialectomized stud male

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showed normal rate of pregnancy (Group IV). The majority of females in which implantation failed returned to oestrus after 3-4 days of resumption of feeding.

Results indicate that ablation of preputial gland does not inhibit production of stud male pheromone(s). Food-deprived females housed with preputialectomized stud males exhibited significant reduction in implantation failure as was seen in food-depreived females housed with intact stud males. It is obvious that the production of stud male pheromone which plays a crucial role in the protective effect on implantation in food- deprived females is not altered by removal of preputial gland. Even though the involvement of preputial gland for the elicitation of releasing pheromonal effects has been proved beyond any reasonable doubt, the involvement of preputial gland in the primer pheromonal effects has been controversial. The present findings confirm that removal of preputial gland did not abolish the production of the pheromone involved in the male induced implantation failure[10] and in the male induction of oestrus[11]. Further, the present study underscores that olfactory cues of stud males involved in leuteotrophic effect in nutritionally-stressed females was not under control of preputial gland. Hence, involvement of preputial gland in the produciton of stud male originating pheromone which provides protection on pregnancy in food deprived females has been ruled out.

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Use of fertilisation protocols to enhance hatching percentage with cryopreserved milt of *Cyprinus carpio*

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Abstract Spermatozoa of common carp *Cyprinus carpio* were cryopreserved and viability was tested under different fertilisation protocols. With different activating solutions, the motility of thawed and fresh milt were evaluated. The pH of the fresh milt varied from 7.5 to 8.5 and the extender used for cryopreservation was found to activate the sperms at higher pH. Higher hatching percentage was observed with 1.5% Sodium sulphite, Diluer 532 and aquarium water. The reduced hatching percentage with well water and extender 'CCI', were correlated with the reduced percentage of motile sperms on activation of the thawed milt with these solutions. Dry mixing of thawed milt with eggs for 30/45 sec were found to be resulted in higher hatching percentage than 10 / 90 sec. The present study indicates that when cryopreserved milt is used, changes in fertilisation protocol can alter the hatching percentage.

(**Keywords**: *Cyprinus carpio*/ cryopreservation/ milt/ fertilisation)

The common carp *Cyrpinus carpio* is one of the widely cultured species. However, work on cryopreservation of carp spermatozoa is comparatively less than other widely cultured species like rainbow trout. Attempts to cryopreserved common carp sperm have either failed[1] or resulted in low larval hatching percentage[2,3]. Kurokura *et al.* reported successful cryopreservation of common carp[4], but even after more than ten years of publication of this article as indicated by Billard *et al.*, successful cryopreservation of common carp spermatozoa is limited[5]. Our trials with cryopreserved milt of common carp have shown a high degree of variability between experiments. The present study was undertaken to determine the reason behind this variability and to test how variations in fertilisation protocols can be used to enhance the hatching percentage when cryopreserved milt samples are used.

For freezing, milt was collected from individual specimens of *Cyprinus carpio* (n=203; total weight 300-400g) caught from wild. Milt from each individual was stripped into separated plastic boxes held over ice taking care to avoid contamination of water, blood, urine and faeces. Milt samples exhibiting more than 80% motile sperm were pooled and used in freezing experiments. The pooled milt was mixed with extender CC1 containing $NaHCO_3$ 20 mg, NaCl 750 mg, KCl 20 mg, $CaCl_2$ 20 mg/100 ml of distilled water. The final ratio of milt : extender : DMSO was 2.0 : 3.5 : 0.5. Extended milt was sucked in 0.5 cc. french medium straws. After an equilibration of 10 min at 5°C, milt was frozen over liquid

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nitrogen (LN_2) vapour for 10 min[6], before plunging into LN_2. The samples were stored in LN_2 and thawed 3 months after storage. To study the effect of various solutions on motility of spematozoa, both raw and cryopreserved (Pooled)milt samples were treated with different media. For cryopreserved samples, thawing was done rapidly by immersing the straws in water bath (35°C) for 20 - Sec, after a brief exposure (5 sec) to air at 24°C. Percentage of motile sperms upto nearest 10% was assessed[7] under microscope (400x) using the following activator solutions. The scoring system was slightly modified to have scores at equal intervals of 10%[7].

(1) Tapwater - pH 7.5 (2) Water from fish aquarium -pH 7.5 (3) 1.5% Sodium sulphate - pH 8.5 (4) CC1 extender4 - pH 7.5. (Though CC1 is an extender, some of our earlier experiments with common carp milt showed activation of milt preserved in CC1: DMSO mixture on thawing, without addition of activator. Hence CC1 was selected for this experiment). (5) "Dilueur-532" -pH 8.5 (manufactured by M/S Sanofi,, Sante Animale, Libourane, France. To prepare a working solution, 123 mg of this salt mixture was dissolved in 10 ml of distilled water).

All motility evaluations were carried out in duplicate or triplicate and the average values are presented in Table 1.

The sperm density in raw milt samples were also determined using Neubaeur haemocytometer and it varied from 15.98 to 23.51×10^9 sperms/ml ($19.40 + 2.3 \times 10^9$/ml, mean ± S.D.). The values fall within the range of sperm concentration reported for common carp from elsewhere[8]. The pH of fresh milt samples were also recorded (Table 1).

Gravid females of common carp of about 350g were injected with pituitary at 3mg/kg in two doses after checking the stage of egg maturation in samples drawn with catheter nine hours after first injection. Eggs were stripped into individual containers and lots from two females with good quality eggs were pooled. Frozen straws were thawed as mentioned earlier. The thawed milt from two straws were poured over lots of about 100 eggs and 'dry' mixed for 30 sec. Then 0.4 ml activator solution was poured and mixed for 1 min. To this, 2ml of water was added to remove excess milt which was decanted. The eggs were incubated in plastic bowls with 1000ml of water untill hatching. A control lot of eggs were fertilised with 50 ul. of fresh milt pooled from three males. All treatments were carried out in duplicate or triplicate. Two experiements were carried out for evaluating the activating solutions and one experiment to determine the optimum period of dry mixing from among the tested 10, 20, 45 and 90 sec. The fertilisation rate was determined by recording live eggs 24 hours after fertilisation and eyed stage when the developing eggs had developed eyes. Hatching rate was based on the nubmer of larvae obtained in relation to the eggs used in each replicate.

The pH of milt collected on diferent occassions ranged from 7.5 to 8.5 (Table 1). Such pH variations have been reported in land locked salmon[9] and tilapia[10] during the milting period. At all pH values, fresh milt activated with "Diluer 532", sodium sulphite borewell and aquarium water exihibited 100% motile sperms. All the milt samples were of free-

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Table 1– Motility percentage of fresh and thawed *Cyprinus carpio* spermatozoa on activation with different activating solutions.

Sl. No.	Activator	Fresh milt(pH)				Thawed milt
		7.5	8.0	8.2*	8.5	
1.	Diluer 532 pH 8.5	100	100	100	100	80
2.	Extender CC1 pH 7.3	0.0	10	80	100	0.0
3.	Sodium Sulphite pH 8.5	100	100	20	90	80
4.	Bore well water pH 7.5	100	100	100	100	30
5.	Aquarium water pH 7.5	100	100	100	100	80

* Highly viscous milt.

flowing consistency except one (pH 8.2) (Table 1), which was highly viscous. The commonly used extender CC1 was found to activate sperms in fresh milt. This activation was found to be dependent on the pH of milt. At milt pH 7.5 there was no activated sperm while at pH 8.5, 100% activated sperm were observed. This could only be due to the interaction between milt pH and extender CC1. In the case of thawed milt, motility rate was 80% with all activators except with borewell water and extender CC1 (Table 1).

With extender CC1 as the activating media, the fertilisatiion rate was high (Table 2), but subsequently there was mortality and only 26 % of the fertilised eggs hatched out. On the other hand, when aquarium water was used as an activating solution, all the fertilised eggs hatched. This contrasting pattern of mortality after hatching indicates that under certain fertilisation conditions, a considerable fraction of the thawed sperm get damaged. The damaged sperm still retain capacity to fertilise and the developing larvae might die before hatching.

High hatching rates were observed with Dilueur 532, aquraium water and sodium sulphite (Table 2). The performance of Dilueur-532 was equally good with frozen milt of Indian cyprinids in our laboratory (results unpublished). There is a wide disparity in hatching rates, when sodium sulphite was used (Table 2). Further experiments are needed to prove the efficacy of this solution as an activator.

The duration of 'dry' mixing before addition of activating solutions was found to in-

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Table 2 – Effect of activating solutions on *Cyprinus carpio* cryopreserved milt viability.

Exp.	Activator	Fertilisation rate(%)	Eyed stage rate(%)	Hatching rate(%)	Hatching as(%) control
	Tap water	9.6±8.1	6.6±3.8	6.6±3.8	18
	Diluer 532	31.6±14.8	31.6±14.8	30.5±13.2	83
I.	1.5% Sodium sulphite	24.5±14.8	14.9±3.7	14.9±3.7	41
	Control	50±13.9	42.9±13.5	36.8±10.2	–
	Aquarium water	22.8±0.6	22.8±0.65	22.8±0.6	91
	Diluer 532	39.3±5.2	31.4±7.5	23.4±6.6	93
II.	Sodium sulphite	46.8±7.8	36.4±5.3	27.4±7.8	109
	Extender CC1	40.5±17.0	25.7±10.1	10.7±4.0	43
	Control	38.2±7.2	34.1±5.3	25.1±5.2	–

Table 3 – Viability of cryopreserved *Cyprinus carpio* milt under different durations of 'dry' mixing and activated with 'Diluer'' 532.

Sl. No.	Duration (SEC)	Fertilisation rate (%)	Eyed stage rate(%)	Hatching rate (%)	Hatching as % of Control
1.	10	18.2±9.7	16.3.±9.7	11.5±4.2	46
2.	30	39.3±5.2	31.4±7.5	23.4±6.6	93
3.	45	36.0±8.6	36.0±7.2	27.0±2.0	108
4.	90	31.5±3.4	26.8±1.1	14.7±4.1	59
5.	Control	38.2±7.2	34.1±5.2	25.1±5.2	–

- Activator solution used "Dilueur - 532".

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fluence hatching percentage with the maximum values observed at 30 and 45 secs (Table 3). The lower duratin of 10 sec might not be adequate for eggs to be fertilised and longer duration of 90 sec might have resulted in structural changes in the integrity of sperm before fertilisation is completed. Osmolality dependent alterations have also been reported to occur in the permeability and structure of carp sperm plasma membrane[11]. In *Thymallus thymallus* ultra structure studies have shown a time dependent change on dilution and thawing of cryopreserved milt[12]. A decline in the fertilising capacity of cryopreserved sperm with time after thawing has been reported in rainbow trout[13] and common carp[14].

The results indicate that by using activating solutions and controlling the duration of fertilisation, hatching percentage of crypreserved milt can be enhanced.

The authors acknowledge Dr. P. Das, Former Director, NBFGR for his encouragement during present investigation.

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Erythrocyte osmotic fragility in different vertebrate species

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Abstract A study was undertaken to comparatively analyse the erythrocyte osmotic fragility (OF) of two mammals (man-*Homo sapiense sapiense*, rat-*Mus musculus*), bird (fowl-*Gallus gallus*), a reptile (girgit-*Calotes versicolor*), amphibia (frog-*Rana tigrina*) and fish (gurrie-*Channa punctatus*). Wide variations were observed in the OF profile and mean erythrocyte fragility (MEF) of different vertebrate species. The observed changes of OF in different species suggest adaptive changes in erythrocyte in response to changing physiological and environmental conditions.

(**Keywords** : erythrocyte/ osmotic fragility/vertebrates)

Red blood cells (see cover page) are concerned with oxygen transport from lungs to various tissues. The erythrocyte metabolism in man and other animals shows great variation, particularly with respect to oxygen affinity and the interaction of hemoglobin with 2,3-diphosphoglycerate. Many of the human complex congenital and hereditary forms of hematological abnormalities e.g. thalassemia, hereditary elliptocytosis, and G-6-PD dificiency have not yet been recognized in lower animals[1]. All these examples emphasize the importance of comparative approach to hematological interpretations.

The erythrocyte osmotic fragility (OF) is frequently used as a measure of erythrocyte tensile strength and is related to cellular deformability[2]. The importance of OF estimation lies in the fact that this hematological parameter gives information about the total status of red cell metabolism and membrane stability[3]. The present work has been undertaken to study the OF profile of erythrocytes in animals belonging to mammalia (albino rat, Charles Foster strain - *Mus musculus* (Linn.); man - *Homo sapiense sapiense*), aves (fowl - *Gallus gallus*), reptilia (girgit - *Calotes versicolor*), amphibia (frog - *Rana tigrina*) and pisces (gurrie - *Channa punctatus* (Bloch)).

Collection of blood : Blood samples were collected from various animals following safe bleeding procedures adopting established techniques[4]. Venous blood from healthy human volunteers was collected for experiments with informed consent. Heparin (10 units/ml) was used as an anticoagulant during blood collection. In case of animals, special care was taken not to excite them prior to bleeding. Collected blood was stored at 4°C and used for osmotic fragility experiments within 3 hours.

Determination of osmotic fragility of erythrocytes : Heparinized blood was added to hypotonic solutions of varying concentration of phosphate buffered NaCl (0.85%-0.10%) in

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the proportion of 1 to 100 and the extent of hemolysis was measured colorimetrically at 690 nm. The procedure was the same as described by Dacie and Lewis[5].

The osmotic fragility profile of human erythrocytes and those of rat, fowl, garden lizard (girgit), frog, and gurrie fish is shown in Fig. 1. Although the overall shape of OF profile is sigmoid for all vertebrate species studied, marked differences are observed in fragility of erythrocytes at various hypotonic salt concentrations. Mammalian erythrocytes Human and rat) show higher susceptibility and are more fragile in lower hypotonic salt solutions, whereas erythrocytes from fish and reptile show relatively higher resistance to hemolysis.

Table 1 gives the mean erythrocyte fragility (MEF) of all the animals. The MEF is the salt concentration at which 50% hemolysis is observed for each of the animals studied. Significant differences are observed in the MEF values of mammalian erythrocytes and those from other animals belonging to different class.

Comparative hematology assumes importance since it provides a means of demonstrating basic hematological principles not evident from the study of a single species. Our results show that, not withstanding their primary function of oxygen transport, erythrocytes from different vertebrates (human, rat, bird, amphibia, fish and reptile) show different OF profiles. It is pertinent to mention that only mammalian erythrocytes are enucleated, while those of other animals investigated have nuclei.

The osmotic fragility of erythrocytes is a property that depends on the movement of water into the cells. Changes in osmotic sensitivity has been linked with changes in the intracellular content of monovalent cations, the major osmotically active species within the erythrocyte[6]. Other factors which determine

Table 1– Mean erythrocyte fragility of various vertebrate species. (Values are mean ±S.D.)

VERTEBRATE SPECIES	MEF* (% NaCl)
Rat	0.72 ± 0.01
Man	0.69 ± 0.01
Fowl	0.58 ± 0.01
Frog	0.55 ± 0.01
Garden Lizard	0.45 ± 0.01
Fish (Gurrie)	0.45 ± 0.01

*Mean erythrocyte fragility values were calculated from Fig. 1

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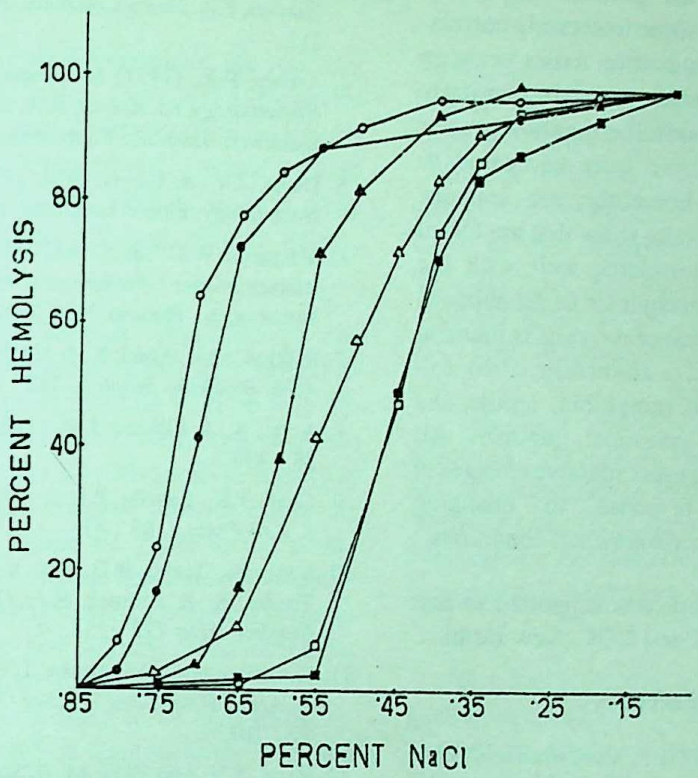

Fig. 1– The erythrocyte osmotic fragility curves of rat – O –, human –●–, fowl – ▲ –, Frog – Δ –, garden lizard (girgit) – ■ – and gurrie (fish) – □ –. Values are mean of 5 to 6 independent experiments.

the OF are complex and include cellular age[7], individual age[8] and change in cell shape[9]. Membrane lipid composition has also been shown to be an important factor that influences erythrocyte OF[10]. Although we have no explanation for the cause(s) of different OF profile observed in all animals, however, the high resistance to hypotonic solutions observed in the increasing order : rat > human > bird > amphibia > reptile > fish is probably an adaptation to variation in ionic strength of the respective blood plasma. An earlier study on amphibian blood has shown that the capacity of red cells to resist osmotic swelling and lysis is affected by cell metabolism and an increase in metabolic rate enhances resistance to hypotonic lysis[11]. Further work is needed to clearly understand the mechanism of resistance to hypotonic lysis in red cells of other animals compared to mammalian erythrocytes. Significantly, it has been reported that *in vitro* insulin treatment of human erythrocytes makes them more resistant to hypotonic lysis[12].

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The erythrocyte OF profiles (Fig 1) and MEF (Table 1) show some interesting correlations. A distinct demarcation exists between aquatic and non-aquatic animals, similarly erythrocytes from poikilotherms show greater resistance to hypotonic lysis compared to erythrocytes from homeothermic animals. Significantly, our results show that the OF of erythrocytes also correlates well with the nitrogen excretion mechanism of the animals. The osmotic resistance of red cells is found to be more pronounced in aminotelic (fish), followed by uricotelic (amphibia, reptile and bird) and ureotelic (mammals) animals. All these correlations suggest adaptive changes in erythrocytes in response to changing physiological and environmental conditions.

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Academy News

1. **68th Annual Session** of the National Academy of Sciences, India and Symposium on "Science and Technology Education – Concerns and Perspectives", would be held from October 23-25, 1998 at Central Drug Research Institute, Chattar Manzil Palace, Lucknow.

Prof. P.N. Tandon, President of the Academy has announced that the Council of the Academy in its meeting held on July 18, 1998 at Allahabad has decided to institute two Awards known as *The National Academy of Sciences, India – Swarna Jayanti Puraskar.* These awards would be given to the young scientists presenting the best research paper in the Sections of Physical Sciences and Biological Sciences at the Annual Sessions of the Academy. During the forthcoming Session of the Academy scheduled to be held from October 23-25, 1998 at Central Drug Research Insititute, Lucknow, the first two scientists would be selected for this award.

2. **Golden Jubilee Celebration of Indian Independence** : The Academy in collaboration with Mehta Research Institute of Mathematics and Mathematical Physics, Jhunsi, Allahabad started the celebration of Golden Jubilee of Indian Independence by organizing lectures. The first lecture of this series was delivered by Prof. A.K. Raychaudhuri, Centre of Relativity and Cosmology, Jadhavpur University, Calcutta, on "Has Time a Beginning or an End" on August 16, 1997 at Allahabad.

The second lecture of the series was organized in collaboration with University of Allahabad and was delivered by Dr. K.D. Broota, Former Professor & Head, Department of Psychology, University of Delhi, Delhi on 'Perception – a matter of representation or construction?' on September 22, 1997 in the Department of Pscychology, University of Allahabad, Allahabad. Prof. Alok K. Gupta presided in the lecture and Prof. R.C. Tripathi introduced the speaker.

The third lecture of the series was delivered by Prof. K.A. Padmanabhan, Director, Indian Institute of Technology, Kanpur on 'Deformation of Nanostructured Materials' on February 6, 1998 in the Department of Botany, University of Allahabad, Allahabad.

The fourth lecture of the series was organized in collaboration with Mehta Research Institute of Mathematics and Mathematical Physics and was delivered by Dr. S.M. Lee, Director (Safety Research and Health Physics), Indira Gandhi Centre for Atomic Research, Kalpakkam on 'The Fast Breeding Programme in India' on March 21, 1998 at Mehta Research Institute of Mathematics and Mathematical Physics.

Professor M.K. Chandrashekaran, Chairman, Animal Behaviour Unit, J.L. Nehru Centre for Advanced Scientific Research, Bangalore delivered the fifth lecture of the series on "Biological Clocks of Bats, Mice and Humans" on July 16, 1998 in the Department of Botany, Allahabad University, Allahabad. Prof. U.S. Srivastava, Past President of the Academy presided over the function.

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The sixth lecture of the series was delivered by Professor Sneh Bhargava, Formerly Director, All India Institute of Medical Sciences, New Delhi on 'A Century of Medical Imaging – The Indian Perspective' on July 17, 1998 in Motilal Nehru Medical College, Allahabad. Prof. P.N. Tandon, President of the Academy presided over the function and Prof. U.S. Srivastava, Past President of the Academy gave a brief account of the current lecture series.

Dr. V.P. Kamboj, Former Director, Central Drug Research Institute, Lucknow delivered the seventh and concluding lecture of the series on 'Herbal Drugs – Opportunity and Scenario' on August 12, 1998 in the Department of Botany, Allahabad University, Allahabad.

Local Chapters of the Academy at Varanasi and Lucknow also organised lectures in the Golden Jubilee of Independence Lecture Series.

3. **Summer School** : The National Academy of Sciences, India, organized a Summer School (June 8-18, 1998) for the students of science of plus two level, drawn from different institutions of Allahabad viz. Maharishi Patanjali Vidya Mandir, Bishop Johnson School, Boy's High School, St. Joseph's Convent, Crosthwaite Girls Inter College, D.P. Girl's Inter College, Jagat Taran Golden Jubilee Inter College and Anglo Bengali Inter College, Allahabad.

The Summer School was coordinated by Prof. U.S. Srivastava; and several senior faculty members viz. Prof. H.S. Mani, Director, Mehta Research Institute (M.R.I.), Allahabad, Prof. Dayal Saran and Prof. H.C. Verma of L.I.T., Kanpur, Prof. T.S. Krishnamurthy of Motilal Nehru Regional Engineering College, Allahabad, Prof. H.C. Khare, formerly Professor of Mathematics & Dean, Faculty of Science, Allahabad University, Prof. S.L. Srivastava, Physics Department, Allahabad University, Prof. Dilip Jatkar of M.R.I., Sri Pramod Pandey of Jawahar Planetarium, Prof. C.B.L. Srivastava, Prof. (Miss) Dipika Kaul, Dr. U.C. Srivastava, Dr. R.R. Tewari, Dr. Krishna Kumar and others of Zoology Department, Allahabad University, Prof. G.K. Srivastava, Prof. D.D. Nautiyal, Prof. B.K. Verma, Prof. Sudhir Chandra, Dr. Sonali Chaturvedi, Dr. D.R. Mishra, Dr. D.K. Chauhan, Dr. Manju Sahni and others of Botany Department, Allahabad University acted as resource persons.

The students were exposed to a variety of experiments and demostrations on linear track experiment, transformers, motors, oscilloscopes, working of Internet, working of planetarium and electron microscope. Lectures and discussion on topics in planetary system, circuit analysis, genetics, neurophysiology, metamorphosis, colour vision, photosynthesis, plant fossils, biofertilizers were also held.

Literature related to the topics of study was supplied to each student. Each student was asked to submit a written critical report on his experience of the various activities in which he/she was involved during the Summer School.

In the brief concluding function, Prof. U.S. Srivastava referred to the enthusiasm shown by the students and also the satisfaction they had recorded in their reports. He assured

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that, based on their comments, the period of the next Summer School would be extended and provision would be made for including some more subject areas of current interest.

A few resource persons, viz. Prof. D. Kaul, Prof. T.S. Krishnamurthy, Prof. Dayal Saran and Prof. S.L. Srivastava also narrated their experiences of interaction with the students.

Prof. H.S. Mani, Vice-President of the Academy, while proposing a vote of thanks to the resource persons and their institutions, stressed that they are the real backbone of the programme and with their help and cooperation the Summer School would become a viable and strong means for enthusing young upcoming students to devote themselves earnestly to the study of science.

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The National Academy of Sciences, India

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SIXTY-EIGHTH ANNUAL SESSION

Central Drug Research Institute, Lucknow
October 23 to 25, 1998

Presidential Address

Prof. P. N. Tandon

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Science and Technology Education: Concerns and Perspectives

"In the rapidly changing world of today, one thing is certain; yesterday's educational system will not meet today's and even less so, the need of tomorrow"

–*D.S. Kothari* (1949)[1].

Introduction

Learning and education were culturally put on the highest pedestal in India long before the advent of civilization in most parts of the world. Our scriptures enshrined these virtually as religion and dignified those involved in such activities as a class above everyone else- a Brahman whose title to respect rested not on any earthy possession or power but on learning and teaching. According to Manu "Wealth, relations, age, good deeds and learning are five titles to respect, of these each succeeding qualification is of greater weight, than each preceding one." It is not generally recognised that notwithstanding claims of science being a gift of the Western civilization, its teaching and training, its value not just as an intellectual exercise but for its practical utility, was recognized in our country at the very dawn of human civilisation. I have no intentions of harping on the ancient glory of our great land but I do wish to demolish the myths that culturally Indians are not attracted to science or lack a scientific temper. From my own discipline-medicine-I may quote Charak, "Sukham Samagram Vijname Ca Pritishthica" (All happiness is rooted in good science). Julius Jully, an authority on Indian culture stated that, "Medicine can now be regarded as the oldest of Indian Sciences, and has proved to be the Science in which Indians specialized first".

It may be of interest to remind the audience of the prevailing views of the Imperial power in the beginning of the century as reflected in the Government of India Resolution on Education in 1904, "Meanwhile the Indian experience of last fifty years has proved .....that the current system of education tends inevitably to accentuate certain characteristic defects of Indian intellect- the development of memory out of all proportion to the other faculties of the mind, the incapacity to observe and appreciate facts and the taste for metaphysical and technical distinctions." However, C.P. Snow, a scholar of sociology of science concluded "....There is no evidence that any country or race is better than any other in scientific teachability: there is a good deal of evidence that all are much alike. Tradition and technical background seem to count for surprisingly little." The risk of revival of

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genetic basis of intelligence has once again begun to cast its shadows with the recent attempts by some molecular geneticists to ascribe most human behavioural traits to genes.

This is not the place for polemics of such debates, suffice it to remind ourselves of the exhortation of Shri Jawaharlal Nehru - the saint-angel of Indian Science ...."It is inherent obligation of a great country like India with its traditions of scholarship and original thinking and its great cultural heritage to participate fully in the march of science, which is probably mankind's greatest enterprise today".

It would be generally agreed that the most valuable resource of a country for its security, sustainable development and self respect consists of trained and continuously learning human beings, an asset whose value appreciates with time. However, there is enough evidence to show that the gap between the S & T knowledge and competence base of the developed and developing countries has continued to widen on all counts, be it those which measure its international competitiveness or its societal functions i.e. to improve health, to generate wealth and to inculcate a scientific temper amongst people at large.

S & T Education: Progress Since Independence

Since independence, the education system in the country has expanded almost exponentially. The number of school-going students, about 12 crores in 1985 (Statistical outline of India 1988-89) is reported to be continuously increasing at the rate of about 3% per year. However, the Government of India in 1986 acknowledged that no more than 60% of schools even have a blackboard, and less than 30% have any kind of library or laboratory facilities (National Policy on Education 1986)[2]. Notwithstanding all efforts including the National Literacy Mission of the Govt. of India[3] the current literacy rate remains at 64.2% for males and 39.2% for females, the average being 52.2%. It may be noted that there are wide differences among different states, with Kerala (89.8%) on the top and Bihar and Rajasthan (38.5% and 38.6%) at the bottom (Central Statistical Organisation Report 1993)[4]. Less than one per cent of students who complete the 10+2 school years go on to science education at college level. While in 1950-51 there were 1,27,000 students enrolled in undergraduate science courses, today the number is more than 10 million. However, the percentage of students opting for science at the undergraduate level was 32% in 1950-51 in contrast to 19% today (Bhide 1993)[5]. Undergraduate education is primarily imparted in large numbers of affiliated colleges rather than in the Universities (University Education in Science, Indian Academy of Science, Bangalore, 1994)[6]. It is common knowledge that barring some exceptions these affiliated colleges are ill-equipped, poorly staffed teaching-shops rather than institutions of learning.

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In 1947, there were only 20 universities in India and 60 national laboratories, today there are more than 200 universities and 400 national laboratories catering to higher education and scientific research. The numbers enrolled annually into higher education in all disciplines has risen from 50 to more than 600 per 100,000 population (Rama Rao 1998)[7]. According to Medical Council of India, there are 141 recognized medical colleges and in addition permission has already been granted to another 15. The total number of admissions to these medical colleges is approximately 16,000 a year. In addition there are a few national postgraduate instistutions like AIIMS, New Delhi; PGI, Chandigarh; SGPGI, Lucknow; SCITMSR, Thiruvananthapuram; NIMHANS, Bangalore.

Information obtained from All India Council for Technical Education (AICTE) revealed that the intake capacity for undergraduate courses in Engineering and Technology increased from 1788 in 1951 to 1,35,840 in 1997. All the IITs enroll approximately 2,000 students at undergraduate level. It is estimated that approximately 10,000 students are admitted in postgraduate (M.E./M.Tech.) programmes. There are 185 institutions, excluding IITs and IISc Bangalore, offering P.G. courses. Thus the annual enrollment of students to higher education was nearly 6.5 million at the end of 1996. However, there was a clear drop in enrollment in basic sciences from 30.0 to 19.6% in a matter of three decades.

A significant percentage of those acquiring higher education in science, engineering and medicine are lost to Indian Science through internal and external brain drain. It is often claimed that India has the third largest scientific and technological manpower in the world (in absolute numbers). However, it comes to only 4.5 per thousand population, as compared to 13 in Indonesia, 17 in Philippines, 83 in Israel, 111.14 for Japan, 122 in the USA, 262.4 in Sweden and 184.8 in Canada. As regards the number of persons involved in R&D, the figure for India comes to 0.27 per thousand population as compared 5.24 for Japan, 5.41 for Sweden and 2.10 for Canada (Srivastava 1993)[8].

Education Policy and Programmes

There has been no lack of awareness of the value of education, including that of S & T as a vital ingredient of national development amongst our policy makers and planners. During the last years of our struggle for independence, the Indian National Congress appointed a National Planning Committee, and one of its subcommittees headed by Shri Jawaharlal Nehru was concerned with planning for S & T. Jawaharlalji as the first Prime Minister of Independent India initiated a series of programmes to rejuvenate and strengthen Indian S & T endeavour. S & T community in India should be grateful to him not just for articulating

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the need for developing S & T but also personally midwifing the birth of a chain of research laboratories and at the same time establishing the University Grants Commission to strengthen higher education. India is probably the first country in the world to have had a National Science Policy (1958) personally steered by the Prime Minister himself[9]. The laudatory aims of the scientific policy formulated four decades ago are as relevant today as in 1958 and hence need to be reproduced here (see Appendix 1).

The Technology Policy Statement of Government of India (1983)[10] identified research and development (R & D) along with S & T education and training of a high order for a "pride of place" for enhancing the technology base in the country. With the exception of some brief periods, successive Prime Ministers were also Ministers for Science.

Starting with the Radhakrishnan Commission on University education (December 1948-August 1949)[1] and the Mudaliar, Mootham and the famous Kothari Commission (1964-1966)[11], several government and non-governmental bodies have periodically addressed the health of S & T in the country. A major effort in this direction was made by the National Council for Science and Technology in 1970s (NCST), followed by the Science Advisory Council of the Cabinet (SACC) and the Science Advisory Council to the Prime Minister (SAC-PM), in addition to the special committees appointed by the Planning Commission at regular intervals. A major effort was also made in mid-eighties in preparation of the National Policy on Education (1986). The National Literacy Mission was launched in 1988. Ten million volunteers are reported to have spread across 448 districts. 234 districts have already moved into the post-literacy stage and 60 into the continuing education stage. Only a few years ago, on the request of the Minister for Human Resource Development, Prof. Yashpal produced a report on school education (not science specifically) "Learning without Burden". Burdened as they are, children today are growing as bonsai, beautiful but suffocated. In spite of the widespread approbation of this report, including by our Parliament, the fate of its implementation remains enmeshed in the cog-wheels of the bureaucratic machinery.

The science academies in the country, whose primary objective has been to promote the development of S & T in the country, have also, from time to time, independently evaluated and made wide ranging recommendations for improving the health of Science & Technology. Without attempting to catalogue these efforts in toto, let me refer to some of the more recent ones with which I had the privilege to be associated. On the initiative of the SACC, at that time headed by Prof. M.G.K. Menon, a meeting was organized at the Indian National Science Academy, New Delhi on September 12 & 13, 1983, to discuss "Excellence in Science"[12]. The Presidents of the three science academies, along with nearly 45 distinguished scientists

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deliberated on the subject, based on nine working papers circulated in advance. There was a general consensus that the S & T enterprise in the country - be it education or research - was not in good health. A series of recommendations to remedy the situation were made to SACC for further action. The SAC-PM after an internal discussion requested INSA to organise a workshop on "Health of Science in India" on April 17-18 , 1986[13]. This was prompted by the feeling that, "There seems to be a widespread view in the country that in spite of spectacular achievements in fields like agriculture, atomic energy and space since independence, the quality of science in India leaves much to be desired." An important question deliberated upon was, "Is the present system of education conducive to quality science?" If not, what can be done to improve the situation? The workshop identified the existing strengths, and the factors impeding quality improvement and made a series of suggestions and recommendations. Science education and research was again discussed in December 1991 by INSA as a part its deliberations on "Role of the Academy: Agenda for Next Decade." At the time of the Diamond Jubilee of INSA, a seminar was held specifically on "Science Education" on 8th January 1994.

I am happy to record that after due consideration the National Academy of Science, India has for several years now, a variety of programmes for promoting science education at all levels-schools, colleges, university. Prof.Uma Shankar Srivastava - one of our past Presidents and a number of other Fellows, need to be complemented for their untiring efforts in this regard. Some of you will remember his thought provoking Presidential Address on "State of Science in Indian Universities" delivered at Bangalore in November 1993[8].

The Indian Academy of Sciences, Bangalore, amongst its many other deliberations and programmes for promoting excellence in Science, had a detailed discussion on "University Education in Science" in December 1994[6]. It has already initiated a new journal, "Resonance" and several other programmes. Current Science, one of the Journals of The Indian Academy, has become an important vehicle for promoting debates, expression of thoughts and detailed studies on various aspects of Science & Technology in the country. Till date, including 1998 itself, a series of publications has come out which includes such topics as "What ails Indian Science"[15], "Decline in interest for S & T training"[16], "Funding basic Science"[17], "Science in India" a scientometric analysis[18], "How relevant is medical research in India"[19], "Medical research on sick list"[20] etc.

The Indian Science Congress, the largest corporate body of Indian Scientists is no less concerned with this subject. The Presidential Address by Prof. M.G.K. Menon delivered on 3rd January 1982 at the 69th Session of ISCA at Mysore on "Basic Research as an Integral Component of a Self-Reliant Base of Science & Technology"[21] is a thought-

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Table 1a

Progress of S & T Expenditure in Different Plan Periods

(Rs. in Crores)

Five Year Plan Period		Plan	Non-Plan	Total
First Plan	(1951-56)	14	6	20
Second Plan	(1956-61)	33	34	67
Third Plan	(1961-66)	71	73	144
Plan Holiday	(1966-69)	47	83	130
Fourth Plan	(1969-74)	142	231	373
Fifth Plan	(1974-79)	693	688	1381
Annual Plan	(1979-80)	208	222	430
Sixth Plan	(1980-85)	2016	1652	3668
Seventh Plan	(1985-90)	5087	3158	8245
Eighth Plan	(1992-97)	11795.13 (Estimated)	N.A.	----

Table 1b

Plan Expenditure on Education

(Rs. in crores)

1st Plan	153
2nd Plan	273
3rd Plan	589
4th Plan	547.51
5th Plan	1143.46
6th Plan	2618.71
7th Plan	7633.13
8th Plan	25413.85

Source : Page 11 to 18 annual Financial Statistics of Education Sector 1997-98, Ministry of Human Resource Development, Deptt. Education, Planning and Monitoring Unit, New Delhi, 1998. Champak Chatterjee, Jt. Secretary, Deptt. of Education. These figures comprise of Centre and States.

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provoking comprehensive statement on this subject. In 1994, the Presidential Address by Prof. P N Srivastava, dealt with "Science in India-Excellence and Accountability"[22]. Prof. Rama Rao in 1998 devoted his address to "Science & Technology in Independent India – Retrospect and Prospect"[7]. As is the tradition of ISCA, the Presidential Address is also on the focal theme of the Congress. The recommendations made as a result of these deliberations are expected to be duly considered by the Department of Science & Technology, Government of India. I have enumerated all this to record that the subject of S & T education in India has been continuously under discussion and scrutiny and yet it remains a matter of increasing concern even today.

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Resource Allocation for S & T

From the First Five Year Plan onwards there has been progressive increase in Central S & T allocations (Table. 1a&b). A mere rupees 20 crores in the 1st Plan increased to Rs.9177 in the 8th plans. There were quantum jumps between 4th & 5th and 7th Plans. The increase in actual amounts, need to be viewed in a different perspective. From a mere 0.17 per cent of GNP in 1958-59 it progressively increased to 0.98 per cent in 1987-88. However, during last decade it has progressively come down to 0.85 per cent which falls far below the 2.5 to 3.0% of the GNP invested by the leading industrialised countries. One has also to take into consideration the rate of inflation and progressive fall in the value of rupee in foreign currency. Major parts of these allocations are devoted to atomic energy, space and defense research. Funds for basic science research or for that matter industrial research remain only a small percentage of the total.

It is also important to realise that the contribution of individual states, as also the industry, remains miserably low, not showing signs of any significant improvement even in recent years. In addition, unlike in many developing countries philanthropic organisations and wealthy individuals barring a few, hardly make any worthwhile contributions to either education or research. In contrast Wellcome Foundation alone contributes an amount equal to the Government's allocations for biomedical research in the UK. The Ford Foundation, Rockefeller Foundation, Carnegie Foundation and hundreds of others in the US are generous contributors to education and research.

In terms of the expenditure on education it has not been possible to get separate figures for science education. In general, in spite of repeated recommendations by various academies, agencies, commissions and even government organizations to increase the overall expenditure on this vital activity to 6 per cent of the GNP, it still remains a distant dream.

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Science & Technology education and research are intricately linked and draw strength from each other. Hence an evaluation of the one can reflect on the state of the other. There can be a number of parameters which could be utilized to evaluate the contributions of any nation's scientific research. These may vary from purely intellectual ones like the number of publications and their impact (Scientometric analysis) or the number of Nobel prizes won, on the one hand, to measures reflecting its contributions to national security, development or wealth on the other. No attempt is being made here, nor is it possible in the time available, to provide an in-depth analysis; however, some general comments based on random observations, may provide a birds eye view of the prevailing scenario.

Let me start with what seems to be quantifiable i.e. the research publications. Starting with Garfield's 1983 analysis of "Science in the Third World"[23] there have been several such studies dealing with various aspects of Indian Science-overall publications, publications on medical research, agriculture science etc. - including the most recent one by Arunachalam *et al.* 1998[18] besides Reddy *et al.* 1991[24], Sahni *et al.* 1992,[25] Gibb 1995[26], May 1997[27] and Raghuram & Madhavi 1996[28]. On the face of it, it may be of some satisfaction to learn from Garfield, the pioneer of Scientometry, that, "India is the giant of the Third World Science". It published 60% of all articles in the Third World scientific press. India also ranked first among Third World publishing countries when impact is taken into account." Similarly according to an article published in 1973 in the Science Citation Index (SCI) which took into account the citation between 1973-78, "India ranks eighth when we consider the number of articles its researchers authored in the International Journals discussed here." There were only two developing countries amongst the top 25, Argentina being a distant second to India. However, considering the impact of Third World articles, only 27 developing countries had an impact of 2.5 or more but India was not one of them. Fifteen years later, Arunachalam and colleagues[18] analyzing India's publications as covered by Science Citation Index 1989-1992 observed, "India is the twelfth largest publishing nation, down from eighth in 1980". It may be of some satisfaction that, "Although most Indian papers appear in low impact journals, the number of papers appearing in leading journals of the world, especially in the areas of physics, chemistry and materials science, is increasing even if only marginally. Also, the number of papers appearing in the foreign journals as a whole, as well as the average impact factor of journals in which Indian scientists have published their work is increasing.....". They argued, "while the slide from eighth to twelfth position, from 2.8% of the world literature to about 2% should be of concern, the increasing use of high impact journals is a welcome trend. It was observed that about 6% of the Indian papers included in SCI 1992 were published in journals of impact factor greater than 3.0 and in

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all 187 papers had appeared in journals with impact factor greater than 5.0. Interestingly most of these papers in high impact journals had come from clinical medicine (67 papers), biomedical research (42) and physics (39). In the four-years studied, India contributed 146 papers to clinical medicine journals with an impact factor greater than 10.00. In several other studies, the overall performance in medical research in India has been found to be poor[24,25]. This has even led to Arunachalam (1997)[19] writing a paper entitled, "How relevant is medical research in India?- A study based on Medline; and Valiathan (1997)[20] writing a commentary, entitled "Medical research on the sick list". In another similar analysis, Raghuram and Madhavi (1996)[28] based on publications covered by SCI between 1981 and 1995, observed a decline in Indian share of the world scientific output by 32%, as a result of which India's world ranking declined to thirteenth in 1995. No other country suffered such a massive decline, except the commonwealth of Independent States (part of former USSR). Even more disturbing was the steep decline in India's rank by citation impact from 57 in 1985 to 81 in 1989. The number of Indian journals included in SCI declined from 36 in 1980 to 12 at the time of this analysis.

These overall national figures tend to hide another glaring fact of Indian Science i.e. wide disparities within the country. The largest number of publications, as well as the majority of those in higher impact journals originate from only a few institutions. Thus an analysis of publications from 128 medical institutions in the country by Reddy *et al.* (1991)[24] revealed that only 6 (4.7%) had over 50 articles per year included in SCI, 33 (26%) had 5 to 50, 43 (38%) had 1 to 5 articles and 41(32%) had less than one. Seven medical colleges had none.

Withstanding the limitations of the analyses mentioned above, these do provide a general impression of the trends at least. Doubts about the real significance of such studies have repeatedly been voiced by several distinguished Indian Scientists like Prof. C.N.R.Rao, Prof.G.Padmanaban, Dr.P.M Bhargava and many others not only in India but by scientists from other developing countries. Gibbs (1995)[26] after a survey of the scientific contributions of the Third World, represented in SCI, commented "The near invisibility of less developed nations may reflect the economics and biases of science publishing as much as the actual quality of Third World Research". While most editors of prestigious international journals and those responsible for publication of SCI stoutly deny this, many of the more than 100 scientists and journal editors from the developing world interviewed by Gibbs pointed to structural obstacles and subtle prejudices that prevented the publications of their research in leading international journals. Christopher Zielinski of WHO commented, "The 2% participation in international scientific discourse allowed by Western indexing services is simply too little to account for the scientific output of 80 percent of the world".[26]

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Concerns & Hopes

It is obvious that a wide cross section of the Indian S & T community is deeply concerned with the state of S & T education at all levels from high school to Ph.D, as also with engineering and medical education. While most undergraduate colleges are woefully ill equipped even for teaching, there is an increasing concern regarding the falling standards in most universities. The once highly rated Universities of Allahabad, Calcutta and Madras present a dismal spectre today. The rapid mushrooming of educational institutions specially those for professional education, in recent years, often created for commercial reasons and with profit motive and not for academic interests has aggravated the condition still further. John Maddox (1984), following an extended visit to India to survey Indian Science commented "Indian University system is certainly the largest in the world but probably the most chaotic..... The wonder is merely that so many young people survive the system, even wresting an education from it".

Yet it is equally important to realise that not only significant numbers survive but often they excel even internationally. Many of our scholars who go abroad for postdoc work are often rated as the best by their peers, including the products of the ivy league institutions of the host countries. Most of those who go for their Ph.D. acquire it in the shortest possible time and with credit. This only indicates that their basic education in India could not have been all that poor. No doubt those who go for such studies are usually the better ones. Is it not a fact that the back bone of the most creditable achievements of Indian S & T, be it in agriculture, space, atomic energy, chemical and pharmaceutical industry, information technology including software development is provided by products of the same system? Even at the school and college level there are some creditable achievements. India won at least 2 gold medals and 2 silver medals this year at the international mathematical Olympiad. Students from a school in Lucknow won prizes at the international robotics competition two years running.

The credit may go to the individual talent and efforts rather than the system; nevertheless, it will not be fare to decry the whole system. While all this is no reason for complacency or back slapping, the tendency to overlook what has been accomplished should not make us hypercritical or despondent. Obviously the central question is why are we not doing better, or worse still, why are we sliding down. The general feeling of disappointment referred to earlier could also be a function of expectations. There can be no denial that we could and should have done better considering our cultural and literary heritage, a long tradition for scientific research, the unequivocal demonstration of internationally competitive science carried out under very adverse circumstances by a galaxy of scientists- Ramanujam,

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J.C. Bose, C.V. Raman, Satyen Bose, S.N. Mitra, P.V. Ray, Meghnad Saha, R.N. Chopra, K.S. Krishanan and many others during the early years of this century. Even after Independence, the contributions of Indian S & T in several fields including agriculture, atomic energy, space, remote sensing, chemical technology, information science, defense research, even some aspects of medical and engineering fields provide enough evidence of the continuing traditions and existing potentials. It may be argued that many of the leaders in these fields were trained in institutions of higher learning abroad. Yet, it cannot be overlooked that they were to start with products of our own educational system and a vast majority of those who carried these enterprises on their shoulders did not have the benefit of any exposure abroad. There are, nevertheless, many worrisome concerns. I will refer to only a few.

Social Equity versus Excellence : The socio-economic and political developments both nationally and internationally have posed new challenges as also provided new opportunities. Mere tinkering with the existing system or just quantitative improvement is not going to put us either on the path to international competitiveness or in a position to meet the myriad problems facing the country which require S & T inputs. To meet the dual purpose of excellence and relevance our education system should urgently resolve the two most important issues of (a) social equity versus excellence and (b) the resource requirements. To find a right and nationally acceptable balance between the educational needs of the vast majority of our people, specially those belonging to the underprivileged and deprived classes, on one hand, and the necessity to foster excellence purely on the basis of merit requires all the ingenuity of our political and bureaucratic system. The scientific community has made some specific recommendations in this regard on several occasions mentioned earlier. A working group of the Planning Commission Chaired by Prof. C.N.R. Rao, of which I was a member, prepared a detailed proposal in 1989-90, which in our opinion would satisfy the genuine needs of all with equity and dignity. Without implying that this is the only solution for this very complex and emotional issue, it is only to suggest that it should not be beyond the capability of our educationists, policy makers and administrators to evolve a commonly acceptable programme .At the cost of being misunderstood it must be emphasised that excellence, a necessary ingredient of Science, demands nurturing merit without any compromise.

Cost of education: who is to pay : Too often the excuse given for the present state of our educational system in general and S & T enterprise in particular is lack of resources. It is true that in spite of good intentions the government has not been able to invest as much as is needed to meet the requirements of such a gigantic task. Once again the

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government has promised to enhance the allocation for education to 6% of the GNP. Even if it happens it alone cannot ensure the upgradation of the quality of the education system.

With the rising cost of science education, specially at the college and university level, as also professional education in medical and engineering colleges, the question as to who should pay for it acquires a new urgency. That primary education should be free and school education reasonably subsidized to wipe out the curse of illiteracy from the country is essential, but should higher education be solely the responsibility of the state deserves careful consideration. Not even the richest countries in the world can afford it. It is remarkable that while cost of everything is rising, there has been no upward increase in college and university fees. Social justice demands that no deserving person should be denied opportunity for the highest education befitting his/her talent. But should it imply that those who were capable of paying "exhorbitant fees" for their school education pay only a pittance for higher education. Or since higher education is cheap, hordes of students with no talent or aptitude for higher education crowd such institutions only to add to the existing vast numbers of the educated unemployed.

An equally undesirable situation, at the other extreme, already threatens to muddy our professional education. The uncontrolled proliferation of the so-called capitation-fee institutions has already overtaken the medical and engineering education in several states and the malady is rapidly spreading to others. Those who have money do not need talent to get admitted to these institutions while many meritorious ones without resources and not belonging to the reserved classes are condemned as failures and unable to fulfill their rightful aspirations. Should we not take care of this reverse discrimination. Thus under the pretext of social justice on one hand and dictates of the so-called market forces, on the other, merit is being overlooked. Is it really conducive to excellence - the only yardstick for promotion of S & T?

Without taking a judgmental stance, I only plead that some of these developments need serious consideration at the national level, both in respects to issues of social equity and excellence.

Concluding Comments

There are many other issues which no doubt will be deliberated upon during this symposium by others more qualified to do so, I would still like to mention some philosophical gleanings acquired from a galaxy of wise men. These concern the broad purposes of education

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and the role of the teacher. Socrates preached, " Education is the kindling of a flame and not the filling of an empty vessel". In this era of information technology one is likely to forget that the primary aim of education is to expand individual's intellectual capabilities and not just accumulation of information. Prof.Kothari once warned that information tends to drive away knowledge and knowledge does not necessarily lead to wisdom. He was probably echoing Tennyson's famous line "Knowledge comes but wisdom lingers". The wisdom of Henry Poincare's simile is equally relevant. "Just as houses are made of stones so is Science made of facts, but a pile of stones is not a house and a collection of facts not necessarily science." No matter how complete and valid are the facts taught in our schools today, many of these will be replaced by new ones and most others would be forgotten in a short time. The aim of education should, therefore, be to inculcate the habits of mind, ability to seek rather than store information, a spirit of curiosity and inquiry, courage to investigate and integrity to challenge the blind beliefs. It should foster competitiveness and not conformity, creativity and not imitativeness, and a sense of wonder which forms the very basis of science. There should be concerted efforts to seek and find a method of instruction by which teacher may teach less but learner will learn more. Michael Bishop discussing the purposes and priorities of teaching summarised the priorities as "First to inspire, second to challenge, third and only third to impart information". Lord Ashby echoed similar sentiments. "The commitment of a teacher is not only to transmit knowledge, it is to transmit a tradition of scholarship and attitude to phenomenon.....". Reflecting on the prevailing environment in the country, Gurudev Rabindra Nath Tagore advised, "A teacher can never truly teach unless he is still learning himself. A lamp can never light another lamp unless it continues to burn its own flame". He observed that "the greater part of our learning in the schools has been a waste because for most of our teachers their subjects are like dead specimens of once-living things with which they have a learned acquaintance, but no communication of life and love".

This no doubt is more easily said than done. It requires not only an educational but also a cultural revolution. The example of the efforts of the US in respect to improvement in mathematics and science education should act as a reminder of the difficulties in achieving such goals. In 1989, the American Association for Advancement of Science (AAAS) produced a document "Science for All Americans". This was followed by an education reform effort (Project 2061, 1993), "Bench marks for Science Literacy". In 1995, the National Academy of Sciences, USA issued the National Science Education Standards. It has been observed that, "Despite years of efforts and hundred of millions of dollars, there is scant evidence that the movement to reform US mathematics and science education has significantly improved student learning". (Science 29 August 1997) – this in spite of the push coming from President Clinton himself who has made a cornerstone of his second

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term the goal that US students will be the first in the world in mathematics and science by 2000 AD. However, if the acknowledged most advanced nation as far as S & T are concerned continues to invest in correcting its deficiencies, should not we – who have still to go a long way to be counted amongst the best – also initiate urgent steps to improve our S & T education.

Prime Minister Shri Atal Behari Vajpai, in his address to CSIR recently exhorted, "We must overhaul the system of science education in the country to base it on knowledge and creativity and not on memorizing and examinations...." The scientific community should accept the challenge and once more prove its commitment to excellence.

I sincerely hope that at the end of this symposium we will have an action plan and not a set of pious recommendations.

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GOVERNMENT OF INDIA SCIENTIFIC POLICY RESOLUTION

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New Delhi, the 4th March, 1958

No. 131/CF/57. The key to national prosperity, apart from the spirit of the people, lies, in the modern age, in the effective combination of three factors, technology, raw materials and capital, of which the first is perhaps the most important, since the creation and adoption of new scientific techniques can, in fact, make up for a deficiency in natural resources, and reduce the demands on capital. But technology can only grow out of the study of science and its applications.

2. The dominating feature of the contemporary world is the intense cultivation of science on a large scale, and its application to meet a country's requirements. It is this, which, for the first time in man's history, has given to the common man in countries advanced in science, a standard of living and social and cultural amenities, which were once confined to a very small privileged minority of the population. Science has led to the growth and diffusion of culture to an extent never possible before. It has not only radically altered man's material environment, but, what is of still deeper significance, it has provided new tools of thought and has extended man's mental horizon. It has thus influenced even the basic values of life, and given to civilization a new vitality and a new dynamism.

3. It is only through the scientific approach and method and the use of scientific knowledge that reasonable material and cultural amenities and services can be provided for every member of the community, and it is out of a recognition of this possibility that the idea of a welfare state has grown. It is characteristic of the present world that the progress towards the practical realisation of a welfare state differs widely from country to country in direct relation to the extent of industrialisation and the effort and resources applied in the pursuit of science.

4. The wealth and prosperity of a nation depend on the effective utilisation of its human and material resources through industrialisation. The use of human material for industrialisation demands its education in science and training in technical skills. Industry opens up possibilities of greater fulfilment for the individual. India's enormous resources of manpower can only become an asset in the modern world when trained and educated.

5. Science and technology can make up for deficiencies in raw materials by providing substitutes, or, indeed, by providing skills which can be exported in return for raw materials. In industrialising a country, a heavy price has to be paid in importing science and technology in the form of plant and machinery, highly paid personnel and technical consultants. An early and large scale development of science and technology in the country could therefore greatly reduce the drain on capital during the early and critical stages of industrialisation.

6. Science has developed at an ever-increasing pace since the beginning of century, so that the gap between the advanced and backward countries has widened more and more. It is only by adopting the most vigorous measures and by putting forward our utmost effort into the development of science that we can bridge the gap. It is an inherent obligation of a great country like India with its traditions of scholarship and original thinking and its great cultural heritage, to participate fully in the march of science, which is probably mankind's greatest enterprise today.

7. The Government of India have accordingly decided that the aims of their scientific policy will be:

(i) to foster, promote and sustain, by all appropriate means, the cultivation of sciences, and scientific research in all its aspects—pure, applied and educational;

(ii) to ensure an adequate supply, within the country, of research scientists of the highest quality, and to recognise their work as an important component of the strength of the nation;

(iii) to encourage and initiate, with all possible speed, programmes for the training of scientific and technical personnel, on a scale adequate to fulfil the country's needs in science and education, agriculture and industry, and defence:

(iv) to ensure that the creative talent of men and women is encouraged and finds full scope in scientific activity;

(v) to encourage individual initiative for the acquisition and dissemination of knowledge, and for the discovery of new knowledge, in an atmosphere of academic freedom; and

(vi) in general, to secure for the people of the country all the benefits that can accrue from the acquisition and application of scientific knowledge.

The Government of India have decided to pursue and accomplish these aims by offering good conditions of service to scientists and according them an honoured position, by associating scientists with the formulation of policies, and by taking such other measures as may be deemed necessary from time to time.

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The National Academy of Sciences, India

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SIXTY-EIGHTH ANNUAL SESSION

Central Drug Research Institute, Lucknow
October 23 to 25, 1998

SECTION OF BIOLOGICAL SCIENCES

Presidential Address

Prof. M. Vijayan

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Structure, hydration, plasticity and function of proteins

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Introduction

Structural biology, which is concerned with the structure, interactions and function of biomolecules, forms an integral and important component of modern biology. The method of choice for elucidating biomolecular structure and interactions has been, for several decades, macromolecular crystallography. Indeed the most spectacular applications of X-ray crystallography in recent times have been made in biology. In fact, most of what we know today of the structure, assembly, interactions and, to a substantial extent, functions of biomolecules, has been derived from X-ray crystallographic investigations. Although protein crystallography was born in 1934 when J.D. Bernal and Dorothy Crowfoot (Hodgkin) recorded the X-ray diffraction pattern from the crystals of pepsin (Bernal and Crowfoot, 1934), the first protein structures, those of myoglobin and haemoglobin, were determined by Kendrew, Perutz and their colleagues only by the late fifties and the early sixties (Kendrew et al., 1960; Cullis et al., 1961). Macromolecular crystallography came of age by the seventies. The basic principles of macromolecular architecture also began to be understood by then. The most important of these principles is embodied in the celebrated Ramachandran plot (Ramachandran, Ramakrishnan and Sasisekharan, 1963) which even today continues to be the simplest mode of description and the most important tool of validation of protein structures. The eighties witnessed a second revolution in biomolecular crystallography spurred by technological advances such as those involving position sensitive detectors, computation and synchrotron radiation, and by great advances in other areas of biology such as molecular biology, genetic engineering and immunology. That revolution still continues. There is hardly any area of biology untouched by the results of macromolecular crystallography. Indeed, many of the recent advances in biology at the molecular level have resulted from the synergism between structural biology, particularly macromolecular crystallography, on the one hand and other areas of biology such as genetic engineering and immunology on the other (Vijayan, 1996).

India has had a distinguished tradition in X-ray crystallography starting from the students of C.V. Raman. Traditions from schools abroad, such as that of Dorothy Hodgkin, have also had a strong influence on Indian crystallography. The Indian tradition in biophysics, particularly what would be described today as theoretical and computational structural biology, has also been excellent, thanks primarily to the pioneering efforts of

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G.N. Ramachandran and his associates. Yet, macromolecular crystallography got off the ground in India only comparatively recently for two main reasons. First, work in this area; like that in other areas of modern biology, is relatively expensive and financial support above the minimum critical level became available only after the Department of Science & Technology (DST) initiated its Thrust Area Programme in 1983. In recent years the Department of Biotechnology has also been supporting work in the area in a substantial manner. Only by the late eighties, a truly state of the art data collection facility (at Bangalore) became available in the country. The second reason for the late start of work in the area has been insufficient interactions between crystallographers and biochemists. The first productive, long term collaboration between a crystallographer and a biochemist has been that between A. Surolia and myself which got established in the late seventies and the early eighties. In recent years such interactions have increased substantially and have become widespread.

Serious efforts in the area of macromolecular crystallography started in the late seventies at the Indian Institute of Science, Bangalore, and the Bhabha Atomic Research Centre, Bombay, but, as indicated earlier, the work gathered momentum only in the eighties. In the meantime, Bangalore was identified as a national nucleus for the development of the activity in the country, a role which has now been completed reasonably successfully. The nineties witnessed the initiation of macromolecular crystallography at several centres in the country, in most cases by scientists trained at Bangalore. Work in this area now forms a significant part of research in modern biology in the country. India also has a reasonable presence in the international efforts in the area. On an occasion like the present one, I would have liked to give an overview of the activity at different centres in India in macromolecular X-ray studies. However, the work in the country is so extensive now that it is impossible for me to do so. I plan, therefore, to concentrate on our own efforts in the area. I would not deal with the work of others even at Bangalore, such as that of my colleague M.R.N. Murthy.

Lectins

Lectins are multivalent carbohydrate binding proteins of non-immune origin (Sharon & Lis, 1989). Although originally isolated from plant sources and characterized by their ability to agglutinate erythrocytes, lectins have now been found in animals, plants, bacteria and viruses. Lectins have received considerable attention in recent years on account of their ability to specifically bind cell surface carbohydrates which play an important role in biological recognition. They have been implicated, among other things, in defence against invading organisms, symbiotic association between nitrogen- fixing bacteria and the roots of leguminous plants, and recognition of the host cell by viruses. Their ability to specifically recognise cell surface carbohydrates has led to the widespread use, current and potential, of lectins in biological research and medicine.

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For a long time carbohydrates used to be considered as comparatively uninteresting compounds. It was recognised that cellulose, perhaps the best known polysaccharide which forms the structural component of plants, is the most abundant biopolymer. Importance of carbohydrates as food material was also well recognised. However, the realisation of the role of carbohydrate molecules, especially in association with proteins and lipids, in subtle biological processes occurred only much later. Indeed it turned out that most of the recognitive processes on cell surface are mediated by carbohydrates. Therefore, work on protein-carbohydrate interactions received its due attention only recently. Lectins are archetypal carbohydrate binding proteins and they have been in the focus of research on protein-carbohydrate interactions. The biochemical, physicochemical and crystallographic work at Bangalore on lectins, involving A. Surolia, myself and later K. Suguna and our colleagues, gathered momentum at a time when the field was becoming very active internationally. This has helped us to be in the forefront of the international efforts in the area. The investigations at Bangalore have encompassed several plant lectins from different sources.

Peanut lectin : Unusual quaternary structure, variability in subunit association and carbohydrate specificity

Lectins from leguminous sources are the best studied ones so far. Among them, and indeed among lectins as a whole, peanut (*Arachis hypogaea*) lectin was the first to be established to have specificity for T-antigen (Galβ1- 3GalNac), a chemically well defined antigen linked to malignancy in man. The lectin is a homotetrameric non-glycosylated protein, Mr 1,10,000. Although first crystallized in the early eighties as a complex with lactose (Salunke et al., 1982, 1983), the structure of peanut lectin was finally resolved only by the early nineties. In fact, the progress of peanut lectin crystallography almost paralleled the development of macromolecular crystallography in India. Early attempts to elucidate the structure using the known structure of other legume lectins (Salunke et al, 1985, Mande et al., 1988), the molecular replacement method in crystallographic parlance, failed for reasons which became obvious after the structure was solved. Eventually, the structure was determined by the *ab initio* multiple isomorphous replacement method (Banerjee et al., 1994) and refined at 2.25 Å resolution (Banerjee et al, 1996).

The tertiary structure of peanut lectin is similar to that in other lectins. This fold, which is recognized to be an important carbohydrate binding motif found in proteins other than lectins as well, is illustrated in Fig.1. The most striking regular features of the fold is a six-stranded, nearly flat 'back' β-sheet and a seven-stranded, curved 'front' β-sheet, interconnected by convoluted loops which account for more than half the length of the polypeptide chain. A detailed examination of the peanut lectin structure brought to light a few hitherto unappreciated facets of the legume lectin fold. For example, in the tertiary structure, a short five-stranded sheet plays a major role in connecting the two longer sheets.

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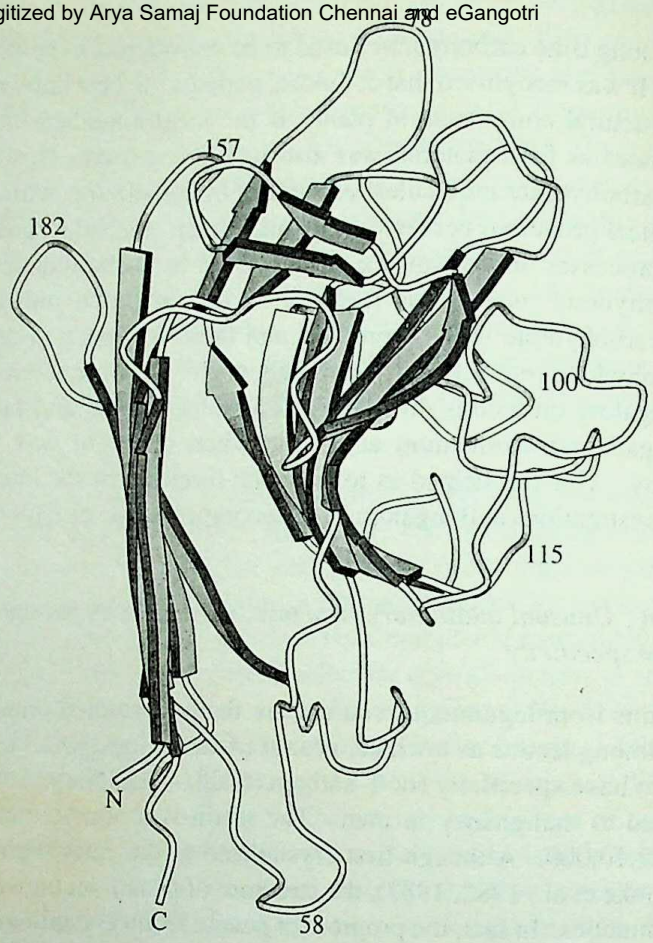

Fig. 1– Tertiary structure of peanut lectin.

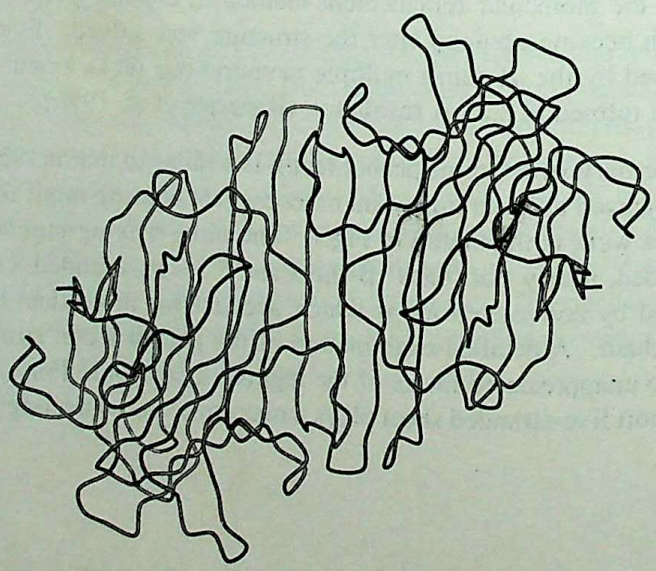

Fig. 3– C trace of a canonical con A dimer. The two monomers are shaded differently.

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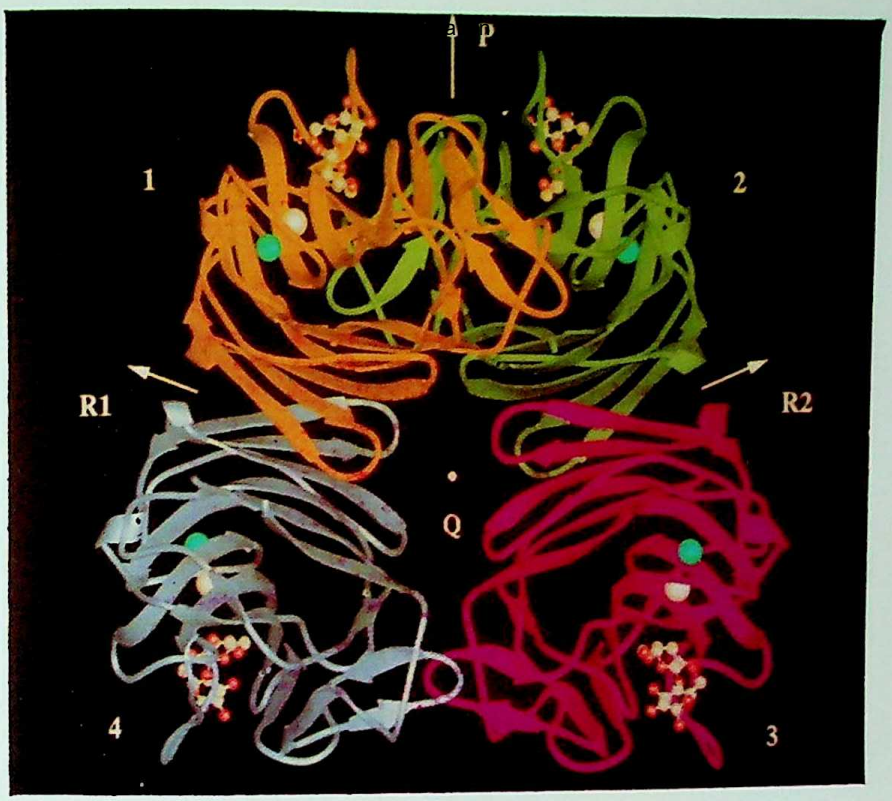

Fig. 2– Quaternary structure of peanut lectin. The four subunits are coloured differently.

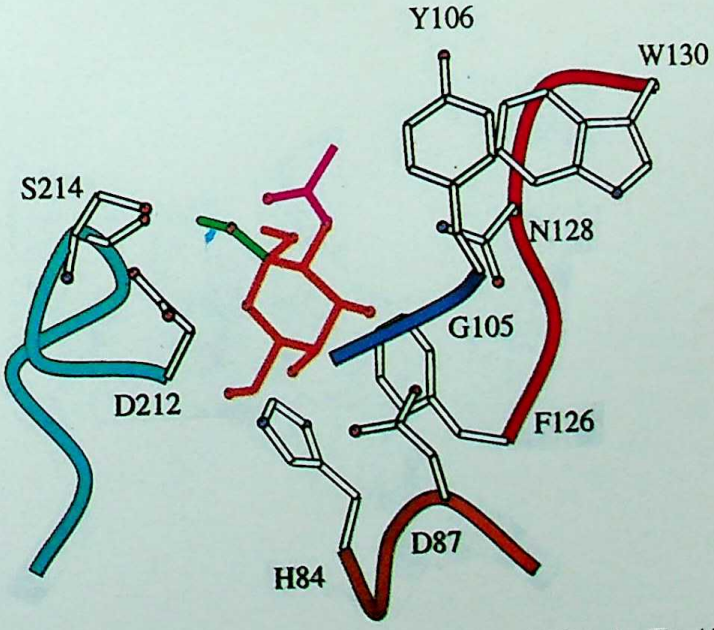

Fig. 9– Carbohydrate binding region of WBAI with the four loops coloured differently. The side chains are in white. Methyl--galactose is in light brown. The modelled ß-methyl group and N-acetyl group are in green and magenta, respectively.

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Furthermore, the loops at the two ends of the seven-stranded sheet curve forward to and interact with each other to produce a second hydrophobic core, in addition to the one between the two large sheets.

The most interesting aspect of the peanut lectin structure is the quaternary association in it. According to the well established principles of Monod and others (Monod et al., 1965), a functional multimeric protein should have a closed structure with an appropriate point group symmetry. Thus a tetrameric protein should have fourfold or 222 (D2) symmetry. Indeed, all tetrameric proteins X-ray analysed till the structure analysis of peanut lectin, conformed to this principle. Peanut lectin, however, does not have fourfold or 222 symmetry. Indeed, it is this unusual nature of its quaternary association that led to the failure of the molecular replacement method in solving the structure of peanut lectin. The lectin tetramer contains a single dyad (P) (Fig.2). The two dimers (subunits 1,4 and 2,3) are related by this axis. The two dimers have internal twofold axes (R1 and R2). However, they are not perpendicular to or intersect with P. Thus, the peanut lectin tetramer has an open structure, in violation of a well-established principle of protein architecture.

All legume lectins are dimers or tetramers made up of dimers. The first legume lectin to be X-ray analysed was concanavalin A (con A) (Hardman & Ainsworth, 1972; Becker et al., 1975). The mode of dimerization in con A involves the formation of a 12-stranded sheet, six strands coming from the back β-sheet of each monomer (Fig.3). Such dimerisation was subsequently observed in many legume lectins and the con A type dimer is often referred to as the canonical dimer. Other modes of dimerisation, involving the back-to-back association of the back β-sheet, were observed in *Erythrina corallodendron* lectin (EcorL) and lectin IV from *Griffonia simplicifolia* (GS4) (Shaanan et al., 1991; Delbaere et al., 1990, 1993). The failure of these lectins to form canonical dimers was attributed to interactions involving covalently bound sugar or a repulsive interaction at the interface of such a dimer. Peanut lectin does not contain covalently linked sugar. Yet, the main interface in the structure, that between the two monomers in each dimer (1,4 and 2,3), is of the GS4 type. An interface similar to that in the canonical dimer also exists (between subunits 1 and 2) in the structure. Thus, the structure of peanut lectin demonstrates that the variability in quaternary association in legume lectins is caused essentially by factors intrinsic to the protein, and not for reasons such as interactions involving covalently linked sugar.

The original structure determination of peanut lectin was carried out with lactose bound to it (Banerjee et al., 1996). Subsequently, the structure of peanut lectin - T -antigen complex itself was analysed (Ravishankar et al., 1997). Structural work on several other complexes involving different sugars is currently in progress. As expected, each subunit binds one sugar molecule at a combining site involving four loops (Fig.4). The details of the protein-sugar interactions in the lactose and the T-antigen complexes are shown in

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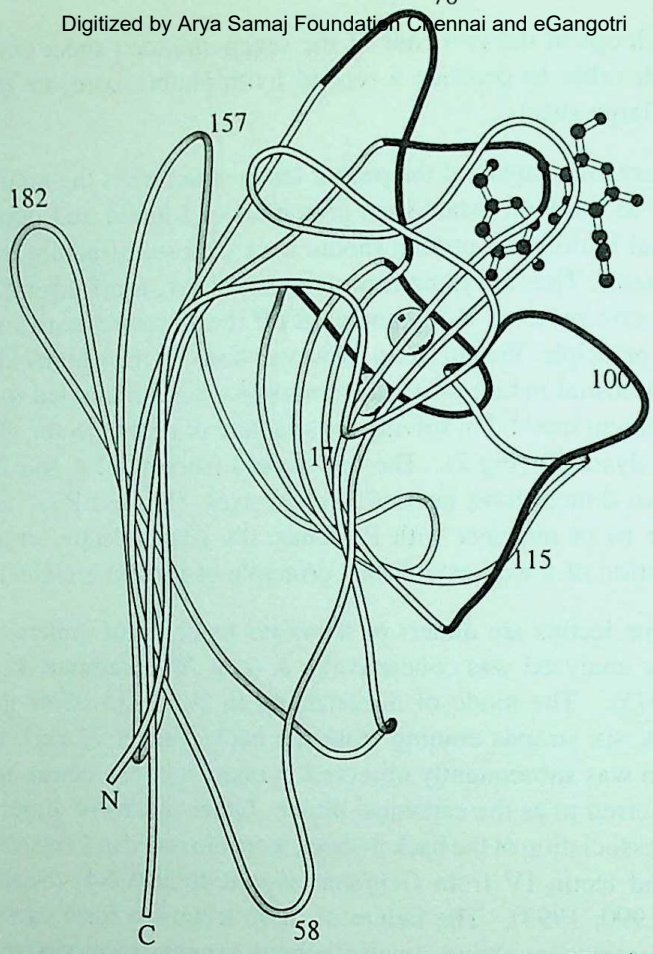

Fig. 4.– C α trace of a peanut lectin subunit along with the bound T-antigen molecule in ball and stick representation. The four loops that make up the carbohydrate binding site are darkened.

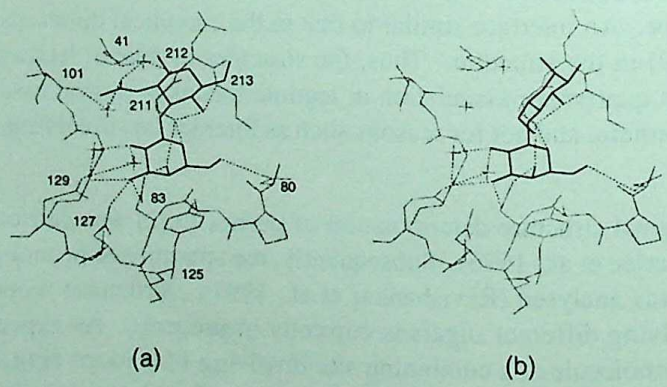

Fig. 5– Peanut lectin-carbohydrate interactions in its complexes with (a) T-antigen and (b) lactose. The carbohydrate molecules are represented by dark lines. The water molecules are shown as crosses. Broken lines represent hydrogen bonds.

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Fig.5. A complete description of these interactions is beyond the scope of this presentation. In general, they are of two types. The first, involving four hydrogen bonds, are common to all legume lectin-sugar complexes. The remaining ones are lectin and sugar specific, and generate the appropriate specificity of interaction. A comparison between the lactose and the T-antigen complexes (Fig. 5(a) and (b)) is of particular interest. Peanut lectin has 20 times more affinity for T-antigen than for lactose. Yet the direct protein-sugar interactions in the two complexes are the same. The only additional interactions in the T-antigen complex are two water bridges between the protein and the sugar. Thus, the specificity of the lectin for T-antigen is generated primarily by two specific water-mediated interactions, probably the first instance where water-bridges have been demonstrated to be responsible for generating specificity in protein-carbohydrate interactions. On the whole, our understanding of peanut lectin-sugar interactions have become thorough enough to permit the re-design of the binding site through protein engineering to enhance the exclusive specificity of the lectin to T-antigen (Sharma et al., 1996)

Winged bean lectin. Further insights into quaternary association and carbohydrate specificity

Basic winged bean (*Phosphocarpus tetragonolobus*) lectin (WBAI) is a dimeric glycosylated protein, Mr 58,000, and is highly specific to blood group A substance and moderately so to B substance, but does not bind to O substance. The structure of its complex with methyl-α-D-galactopyranoside, with two dimers in the asymmetric unit, was determined by the molecular replacement method and refined using 2.5 Å resolution X-ray intensity data (Sankaranarayanan et al., 1993; Prabu *et al.*, 1998). As expected, the polypeptide chain of each monomer has the characteristic legume lectin fold.

WBAI exhibits high sequence homology with EcorL. EcorL does not form a canonical dimer; instead it has a 'hand shake' type back-to-back association of back ß-sheets. It has been suggested that EcorL is prevented from forming canonical dimers on account of the presence of a glycosylation site at the interface (Shaanan et al., 1991). In WBAI, the glycosylation sites are far removed from the intersubunit interface in the canonical dimer. Thus, if interactions involving covalently linked sugar is responsible for the occurence of legume lectin dimers other than the canonical one, then WBAI would form a canonical dimer. However, if factors intrinsic to the protein is responsible for the variability in quaternary association in legume lectins, WBAI would form a dimer of the type found in EcorL in view of the high sequence homology between the two lectins.

The crystal structure shows that WBAI forms an EcorL type dimer (Fig.6). The WBAI structure and our earlier work on peanut lectin demonstrate that legume lectins are an interesting family of proteins in which small alterations in essentially the same tertiary fold lead to large changes in quaternary structure. The different types of legume lectin

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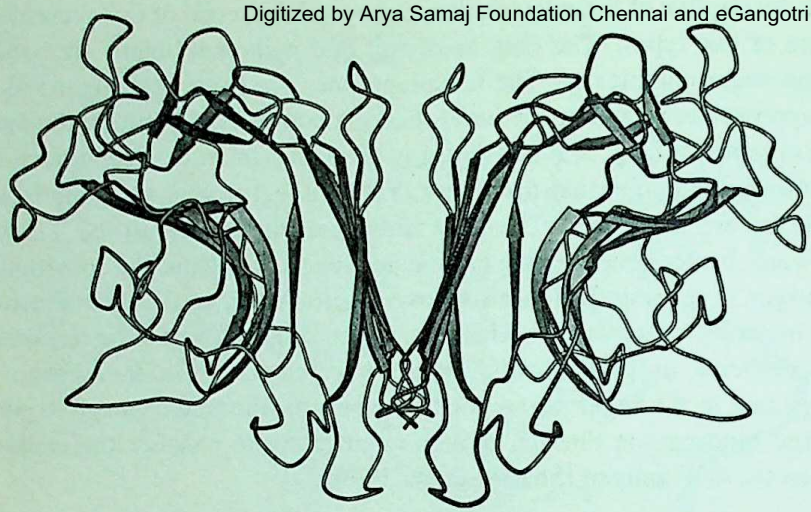

Fig. 6– A WBAI dimer.

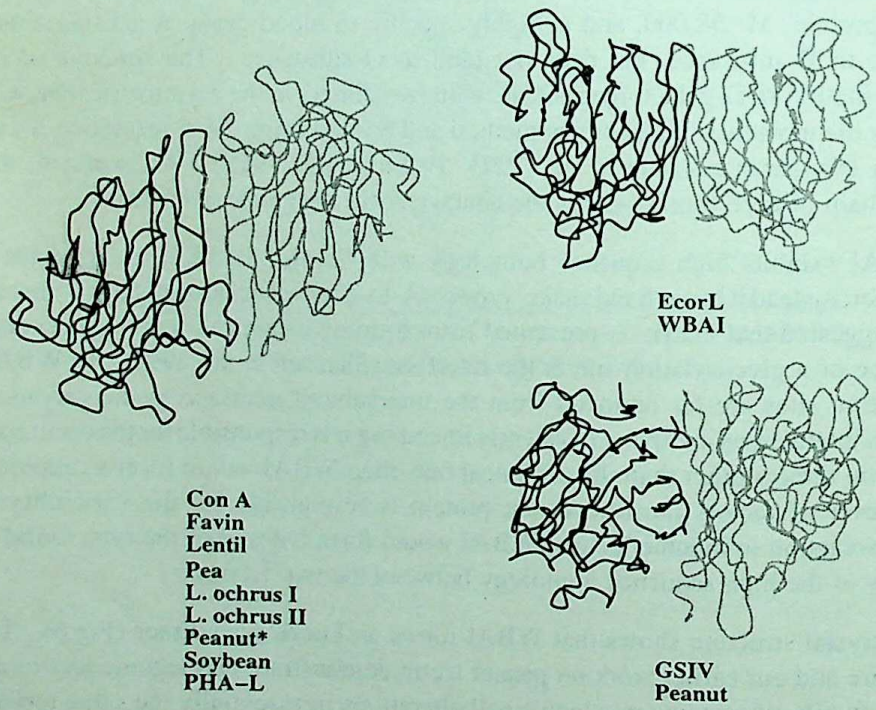

Fig. 7– Different modes of dimerisation in legume lectins. The two subunits in each dimer are shaded differently.

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dimers observed so far are shown in Fig.7. The alterations in the tertiary fold would of course depend upon differences in sequence and therefore the above observation is of considerable relevance in relation to the problem of protein folding. Indeed, legume lectins form an ideal system for studying the effect of sequence variations on quaternary association.

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The details of the lectin-carbohydrate (methyl-α-D-galactose) interactions at the combining site are illustrated in Fig. 8. As indicated earlier, the combining site in legume lectins is made up of four loops. Three of them (residues 78 to 87, 95-117 and 124-134 in WBAI) and the sugar interactions involving them remain invariant among the lectins. The fourth loop (211 to 222) is variable in length and sequence. It is variations in this loop that give rise to differences in the specificities of different legume lectins. This loop is the largest in WBAI, which has an interesting consequence. As shown in Fig.9, a β-linkage, as in lactose and methyl-β-D-galactose, leads to unacceptable steric contacts with the long fourth loop, particularly Ser 214 and Gly 215. The linkage at the terminal sugar in blood group substances A and B is while it is β in the O substance. Naturally WBAI cannot bind the O substance. Further, simple model building (Fig. 9) shows that an N-acetyl group substituted at C2-position of the sugar nestles in a pocket made up of Tyr 106 and Trp 130. The galactose ring has an acetyl group attached at C2 position in substance A and not in B. Hence the higher affinity of the lectin for the A substance. Thus, the structure provides a ready explanation of the general behaviour of WBAI towards different blood group substances.

Jacalin from jackfruit seeds. A new lectin fold and a novel mode of carbohydrate recognition

Jacalin, Mr 60,000, is one of the two lectins found in the seeds of jackfruit (*Artocarpus integrifolia*) which belongs to the Moraceae plant family. Although isolated only recently, the lectin has received considerable attention on account of its interesting biological properties. Jacalin is also highly specific to T-antigen. Each subunit of the tetrameric lectin consists of two polypeptide chains, a long β-chain and a short β-chain, produced by a post translational modification involving proteolysis. The lectin does not exhibit sequence homology with any other protein of known structure.

The structure of jacalin as a complex with methyl-α-D- galactose was solved by the multiple isomorphous replacement method (Dhanaraj et al., 1988; Banerjee et al., 1991; Sankaranarayanan et al., 1996). It revealed a new lectin fold characteristic of the *Moraceae* family consisting of three four stranded sheets (greek key motifs) arranged as the sides of an appropximate triangular prism and loops which connect the strands (Fig. 10). This simple, yet elegant, arrangement has an approximate three-fold symmetry. This symmetry is not, however, reflected in the amino acid sequence. The small β-chain forms an integral

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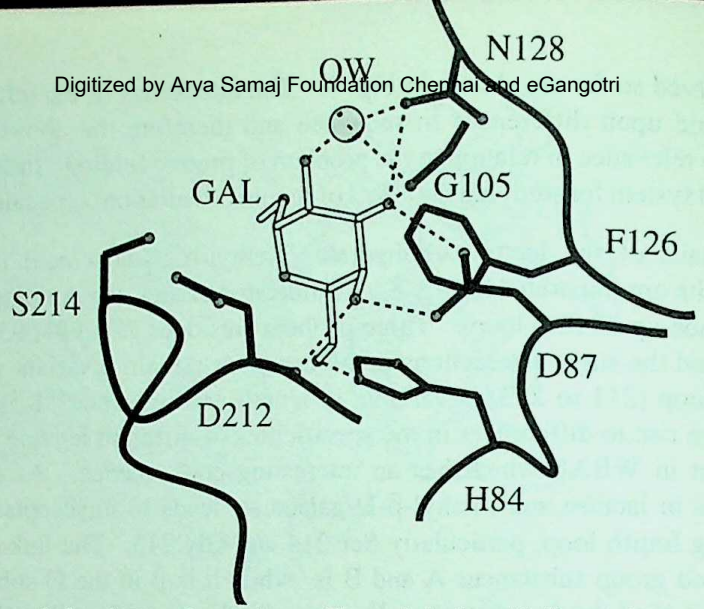

Fig. 8– WBAI - methyl--galactose interactions. The carbohydrate binding region of the protein and the carbohydrate molecule are shaded differently. The ball represents a water molecule.

Fig. 10– Tertiary fold in jacalin. (a) Schematic representation.

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part of the structure as a strand in one of the sheets. The subunits form a tetramer with the expected 222 symmetry.

The carbohydrate binding site is formed by loops at one end of the prism (Figs. 11 and 12). The details of protein- carbohydrate interactions are shown in Fig. 13. Most of the hydrogen bonds with the sugar molecule involve main chain atoms. The only side chain that interacts with the sugar through hydrogen bonds is that of Asp 125. This may facilitate the retention of the carbohydrate binding property of the β-prism fold even when substantial sequence variations occur. The interaction of the terminal amino group (gly 1) of the α-chain, which is generated by a post-translation modification, with O4 of the sugar molecule and its juxta- position with the side chain of Asp 125 are particularly interesting. O4 is axial in galactose. The interaction is not possible if O4 is equitorial as in mannose or glucose. This is the first instance where carbohydrate specificity is generated by a post translational modification. It is also interesting to note that the carbohydrate binding site in jacalin bears no resemblence to that in peanut lectin, although both are highly specific to T-antigen. Thus the same specificity can be generated by entirely different folds containing dissimilar carbohydrate binding sites.

Structures of other lectins

Artocarpin, another lectin from jackfruit seeds, have physicochemical properties and carbohydrate binding specificities different from those of jacalin. However, comparison of the partial amino acid sequence of artocarpin with the known sequence of jacalin indicates close to 50% sequence identity. Artocarpin crystallizes in two forms. Both the crystal structures have been solved by the molecular replacement method using the known structure of jacalin as the search model and one of them partialy refined, confirming that the two lectins are indeed homologous (Suresh et al., 1997). The refinement of the structures is in progress.

Yet another lectin the structure of which has been solved at Bangalore is the mannose-specific agglutinin from garlic (*Allium sativum*), which forms part of a well conserved superfamily of bulb lectins. The protein crystallizes with two molecules in the asymmetric unit. The structure has been solved by molecular replacement using the coordinates of snowdrop lectin as the search model (Chandra et al., 1997) and refined at 2.4 Å resolution. The analysis of the structural results is nearing completion.

Structural diversity and carbohydrate specificity of lectins. A summary

The lectins being worked on at Bangalore encompass three super families, legume, *Moraceae,* and bulb, and a variety of carbohydrate specificities. The unusual quaternary structure of peanut lectin, which violates a well established principle of protein architecture, demonstrates that open structures also need to be considered when dealing with multimeric

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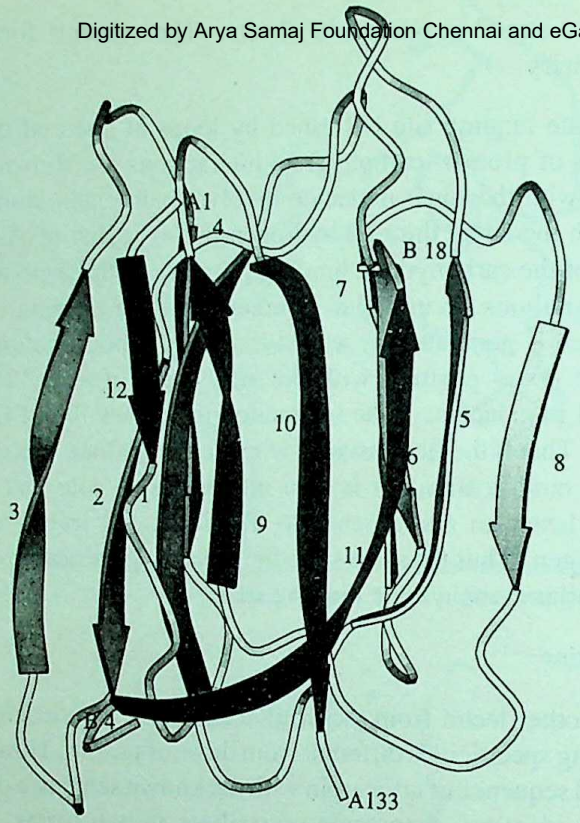
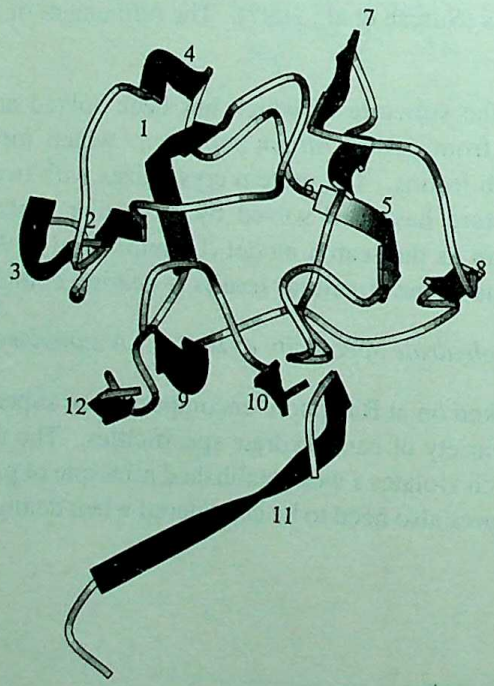


(b) A side view of the ß-prism fold. The three greek key sheets are shaded differently. The strands are numbered



(c) The top view of the fold.

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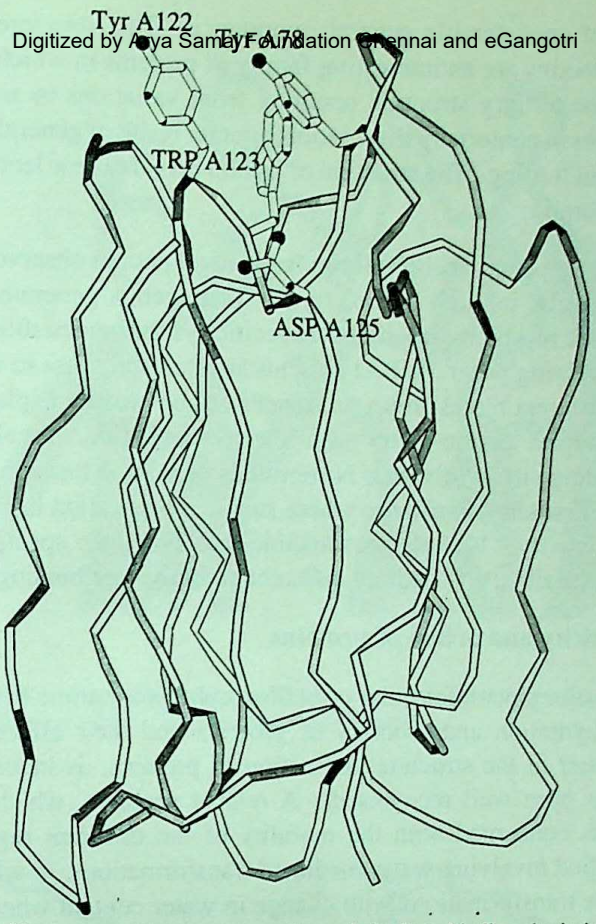

Fig. 11–An illustration of the location of the carbohydrate binding site in jacalin.

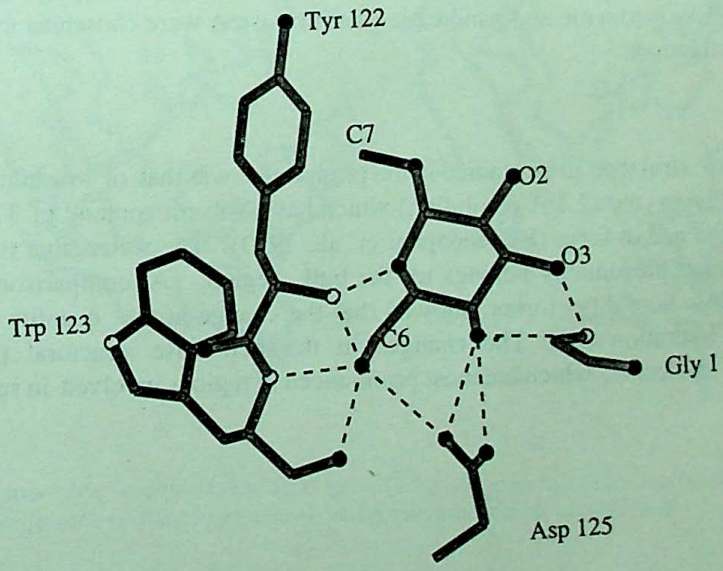

Fig. 13–Jacalin - methyl--galactose interactions.

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proteins, a result of considerable general importance. This structure and that of WBAI show that legume lectins are an interesting family of proteins in which small alterations in essentially the same tertiary structure resulting from variations in amino acid sequence, lead to large changes in quaternary association, another result of general interest particularly in relation to protein folding. The structure of jacalin reveals a new lectin fold characteristic of the *Moraceae* family.

Sugar binding by peanut lectin follows the general pattern observed in legume lectins. However, interestingly, its high specificity for T-antigen is generated by water bridges, perhaps the first case in which carbohydrate specificity has been established to be generated by interactions involving water. WBAI presents an interesting case in which the specificity of the lectin for different blood group substances can be broadly explained in terms of the structure of a complex of the lectin with a monosaccharide. Jacalin exhibits a novel carbohydrate binding site involving a N- terminus generated through a post translational modification, the first known instance where such a modification has been used to confer carbohydrate specificity. It is also remarkable that T-antigen specificity is achieved in peanut lectin and jacalin using entirely different carbohydrate binding sites.

Hydration, plasticity and action of proteins

Another major macromolecular crystallography programme being pursued by us is concerned with hydration and mobility of proteins and their effect on function. The importance of water in the structure and action of proteins, as indeed in those of other biomolecules, has been well recognised. A related problem, which is of considerable current interest, is concerned with the mobility of the different regions of the protein molecule. A method involving water-mediated transformations, in which protein crystals undergo reversible transformations with change in water content when the environmental humidity is systematically varied, was developed in this laboratory to investigate these problems (Fig. 14; Salunke et al., 1984, 1985a). The well known and thoroughly studied enzymes HEW lysozyme and pancreatic ribonuclease A were chosen as model systems in these investigations.

Lysozyme

The first structure to be studied in the programme was that of low humidity (r.h.88%) tetragonal lysozyme (2.1 Å resolution) which has a solvent content of 37.8% as against 39.4% in the native form (Kodandapani et. al., 1990). The water that is lost during the transformation presumably belongs to the bulk region. A comparison of the native and the low humidity forms showed that the change in the quantity of bulk water affects the hydration shell. The changes in the shell cause structural perturbations in the protein molecule, which are most pronounced in regions involved in substrate binding.

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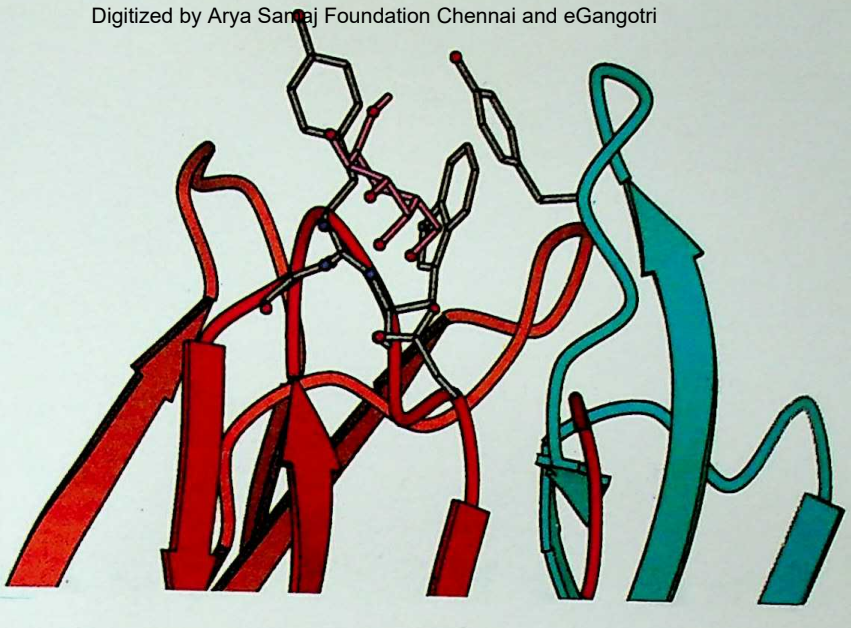

Fig. 12–A close-up view of the carbohydrate binding site in jacalin. The three greek keys are coloured differently. The side chains are dark and the sugar molecule purple.

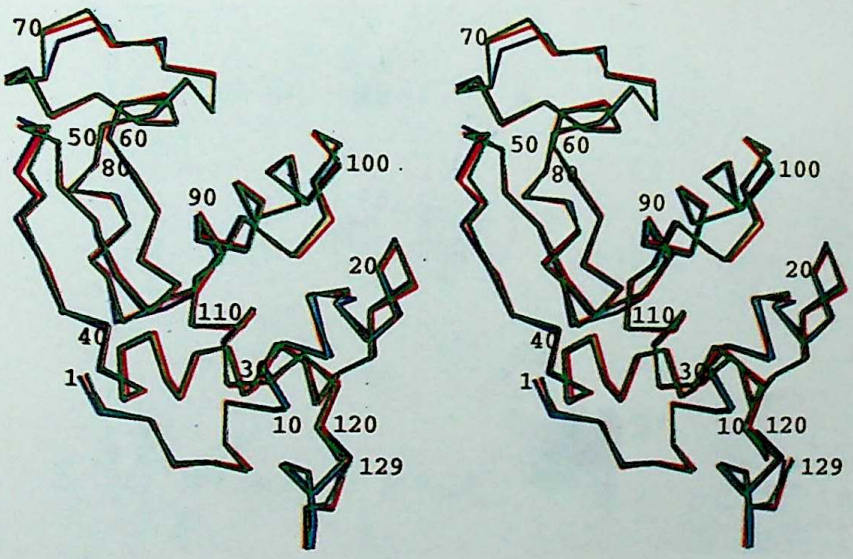

Fig. 15–Stereoview of the superposition of the C atoms in the low humidity (88%) form (blue) and the inhibitor complex (green), on those in a molecule in the native monoclinic crystals (red).

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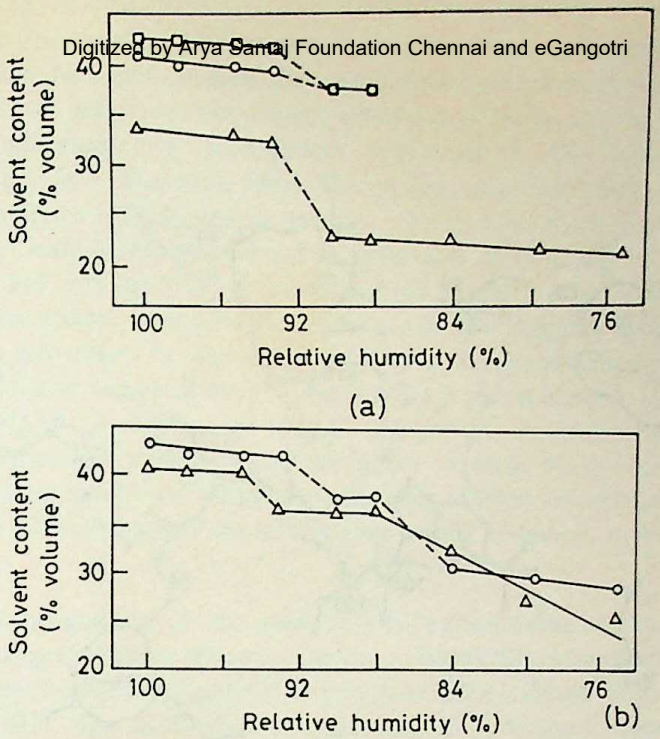

Fig. 14–Variation of solvent content as a function of relative humidity in (a) tetragonal (circle), orthorhombic (square) and monoclinic (triangle) lysozyme and in (b) the alcohol (triangle) and the acetone (circle) forms of ribonuclease A.

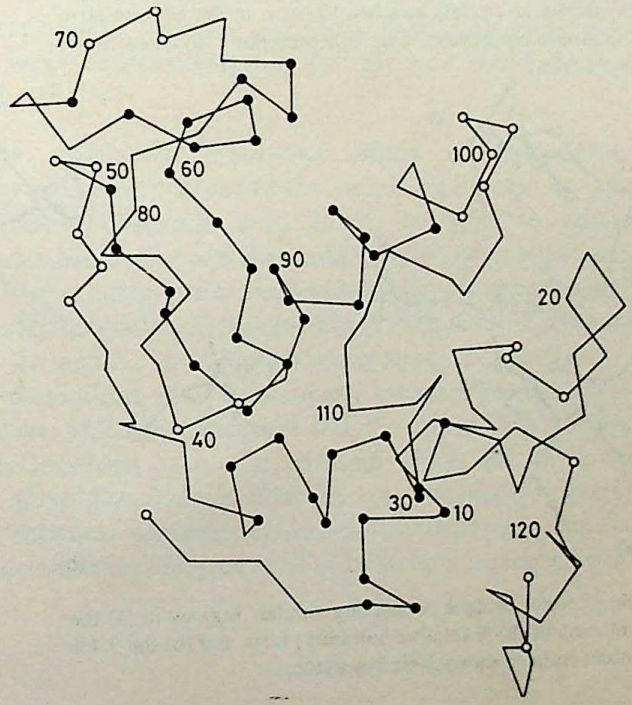

Fig. 16–C positions in the lysozyme molecule. Atoms in the relatively rigid regions and those in the highly flexible regions are denoted by filled and open circles respectively. The others belong to moderately flexible regions.

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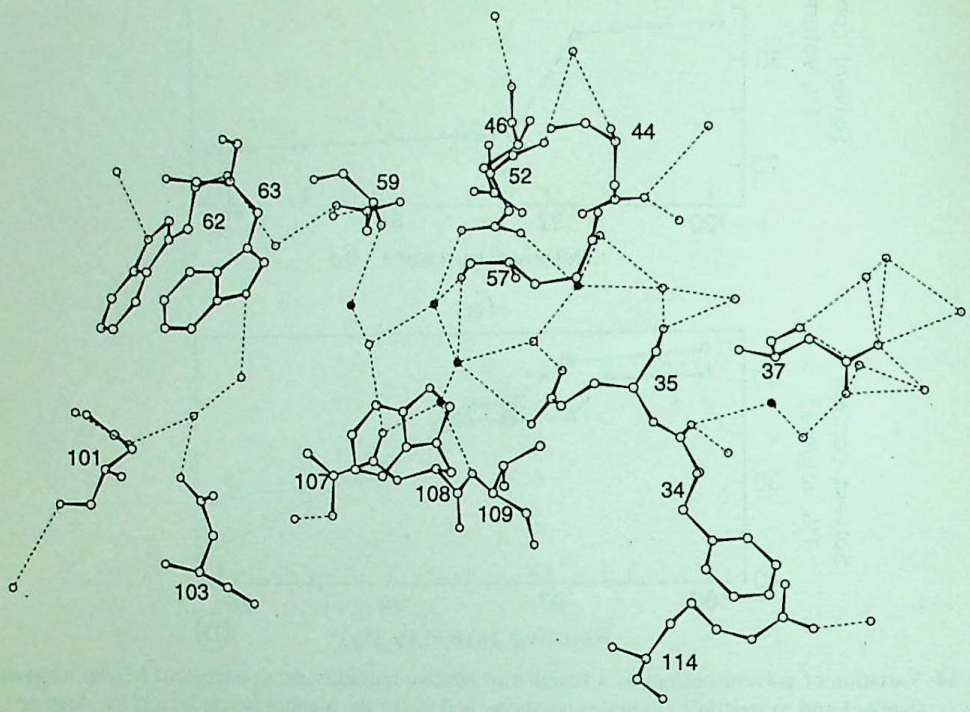

Fig. 17– Residues in lysozyme implicated in substrate binding and water molecules (shown as circles) attached to them in the 88% relative humidity monocliniclysozyme. Circles representing invariant water molecules are filled.

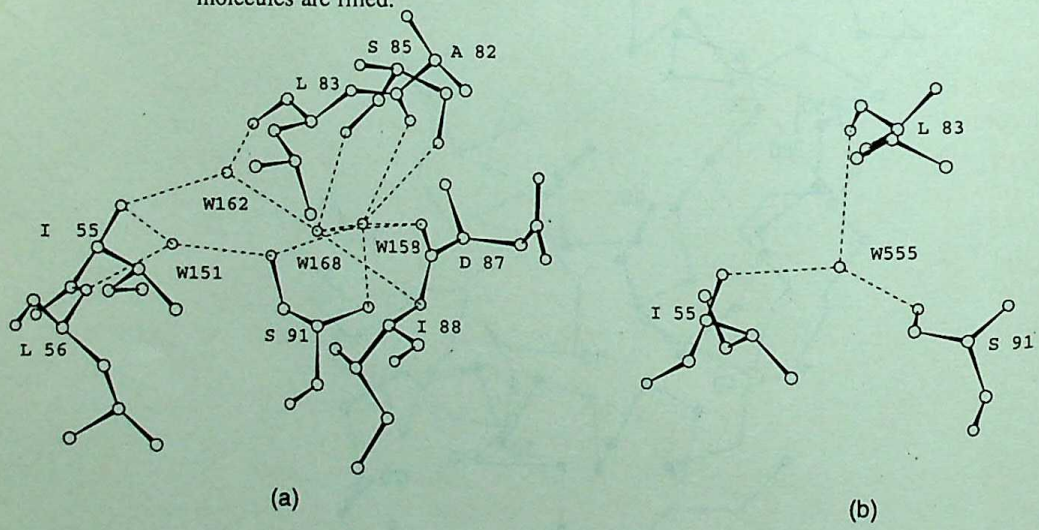

Fig. 18– An example of water bridges connecting similar regions in (a) the 22% solvent content (88% relative humidity) form and (b) the 9.4% solvent content form of monoclinic lysozyme.

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The most spectacular water-mediated transformation is exhibited by monoclinic lysozyme. During the transformation, the water content goes down from 32% in the native crystals to 22% (the lowest solvent content observed till then) in the 88% r.h. form. The two crystallographically independent molecules in the native form become equivalent in the low humidity form. The quality and resolution of the diffraction pattern also improve with the transformation. The known structure of the native form was refined (2 Å resolution) (Nagendra et al., 1996) and the structure of the low humidity form solved and refined (1.75 Å resolution)(Madhusudan et al., 1993). The changes resulting from the transformation from the native to the low humidity forms are pronounced in many of the side chains in the active-site region. A comparison of the C traces of the molecule in the native structure, the low humidity form and an inhibitor complex (Cheetam et al., 1992) (Fig.15) shows that the overall changes in molecular geometry resulting from the water-mediated transformation are similar to those which occur during enzyme action. The same result was obtained using other inhibitor complexes as well. This observation further emphasizes the relationship among hydration, mobility and enzyme action.

A detailed comparison of the available well refined native and low humidity forms of lysozyme using difference distance matrices permitted the delineation of the relatively rigid, moderately flexible and highly flexible regions of the molecule.(Fig. 16, Madhusudan and Vijayan, 1991). The relatively rigid region forms a contiguous structural unit close to the molecular centroid and encompasses parts of the main ß-structure and three -helices. The hydration shell of the protein contains a number of invariant water molecules. Many of them are involved in holding different parts of the molecule together or in stabilizing local structure. Some of the invariant molecules in the substrate-binding region form part of a water-cluster contiguous with the side chains of the catalytic residues Glu 35 and Asp 52. (Fig. 17).

Surprisingly, monoclinic lysozyme retains its crystallinity even when the level of hydration is reduced further below that necessary for activity (about 0.2 gram of water per gram of protein) (Nagendra et al., 1995). In order to gain further insights into the role of water in the stability and the plasticity of the protein molecule and the geometrical basis for the loss of activity that accompanies dehydration, the crystal structures of monoclinic lysozyme with solvent contents of 17.6, 16.9 and 9.4% were determined and refined at 2.1, 2.1 and 2.3 Å resolution respectively (Nagendra et al., 1998). A detailed comparison of these forms with the normally hydrated forms shows that the C-terminal segment (residues 88-129) of domain I and the main loop (residues 65-73) in domain II exhibit large deviations in atomic positions when the solvent content is reduced, although the three-dimensional structure is essentially preserved. Many crucial water-bridges between different regions of the molecule are conserved in spite of differences in detail, even when the level of hydration is reduced well below that required

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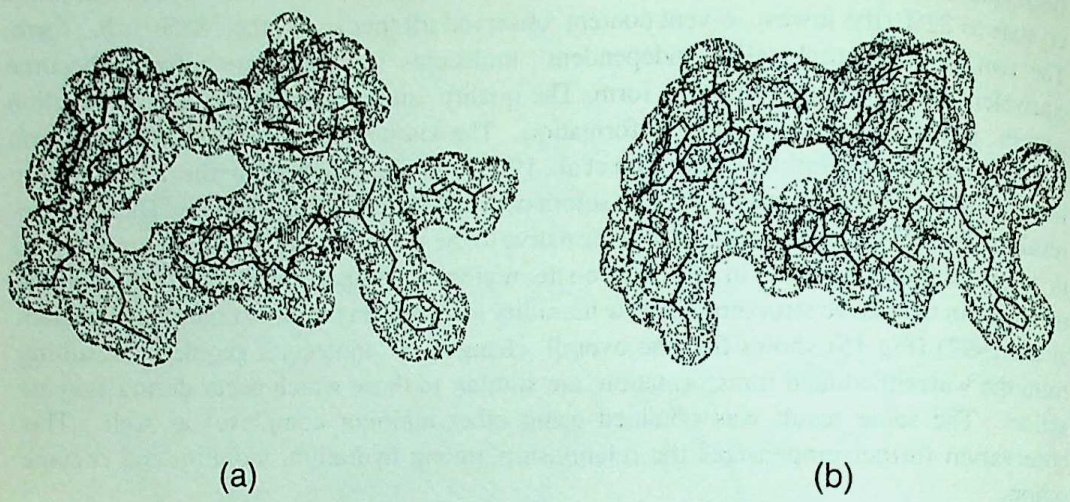

Fig. 19– Solvent accessible area profiles of the active site in (a) the 22% solvent content form and (b) the 9.4% solvent content form of monoclinic lysozyme.

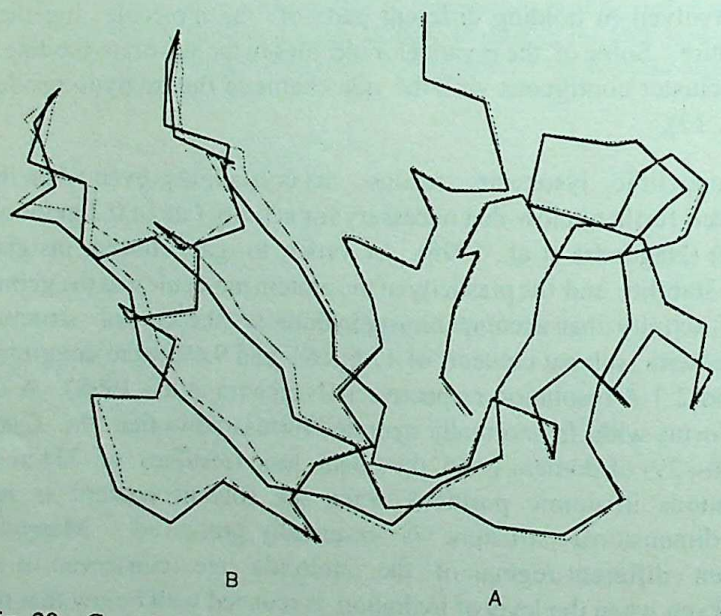

Fig. 20– C representations of the ribonuclease .A molecule in the native (unbroken line) and the 79% r.h. (broken line) forms. The A domains in the two structures have been superposed.

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for activity (Fig. 18). The loss of activity that accompanies dehydration appears to be caused by the removal of functionally important water molecules from the active site region and the reduction in the size of the substrate binding cleft. (Fig. 19).

Ribonuclease A

The well-known monoclinic form of ribonuclease A, grown from alcohol solutions, undergoes two successive water- mediated transformations when the environmental humidity is systematically reduced. The crystal structures of the 88% and 79% relative humidity forms have been refined using X-ray data at 1.5 Å resolution and 1.8 Å resolution respectively (Radha Kishan et al., 1995). The comparison of these structures with those of the native, phosphate-bound and sulphate-bound forms demonstrates that the mobility of the ribonuclease A molecule involves hinge-bending movement of the two domains (Fig. 20) and local flexibility within them, particularly at the terminii of regular secondary structures and in loops. The comparison also leads to the identification of about 30 invariant water molecules in the hydration shell of the enzyme, many of which are again involved in holding different parts of the molecule together and in stabilizing local structure (Fig. 21). It was of interest to compare the native and the low humidity forms with a complex of the enzyme with a transition state analogue, uridine vanadate (Wlodawer et al., 1983). It turns out that the overall changes in the structure during the binding of the substrate analogue are those that result from partial dehydration. This effect is very pronounced in the active site region (Fig. 22).

The above studies have been essentially on one crystal form and its variants. In order to ensure that the general results obtained are averaged over environmental perturbations such as those resulting from crystal packing and the composition of the medium, it is important to examine other crystal forms as well. With this in view, the crystal structures of the native and the 93% r.h. forms of crystals grown from Tris buffer, pH 7.6, with acetone as the precipitant, were analysed at 1.9 Å resolution and at 1.8 Å resolution respectively (Sadasivan et al., 1998). Both forms contain two crystallographically independent molecules. A detailed comparison of these structures with those of the other known crystal forms of the enzyme led to a meaningful delineation of the rigid and the flexible regions of the protein molecule (Fig. 23) and the nature of its plasticity and also the invariant water molecules involved in bridging different regions of the protein molecule. The analysis of the structures show that for a given nitrogen or oxygen atom, the level of hydration increases with accessible surface area, but levels off at an area of about 10 $Å^2$ (Fig. 24). On an average, the level tends to drop when the area increases beyond 20 $Å^2$ on account of the increase in displacement parameters. The analysis also suggests that the van der Waals radii and probe radius normally used in accessible surface area calculations are not appropriate for dealing with all situations.

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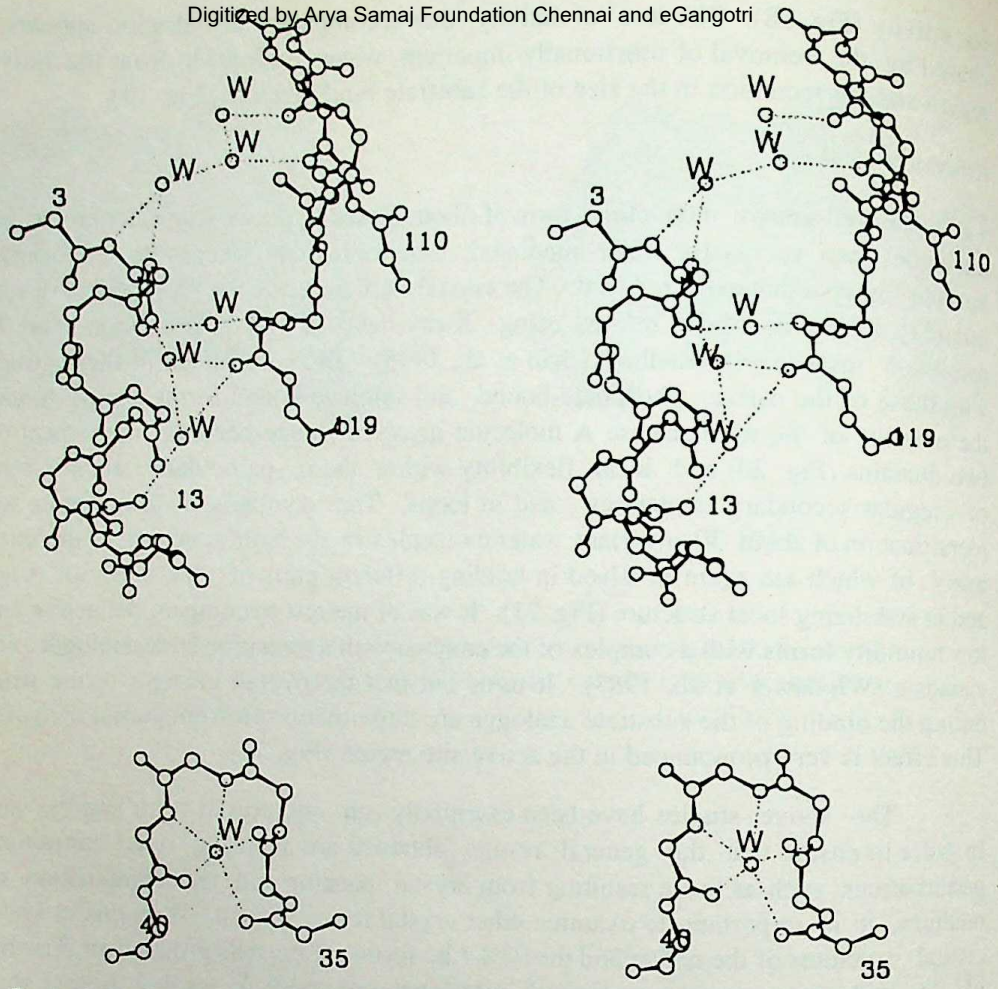

Fig. 21–Stereoviews of examples of stabilization of (top) tertiary structure and (bottom) local structure through water bridges in ribonuclease A.

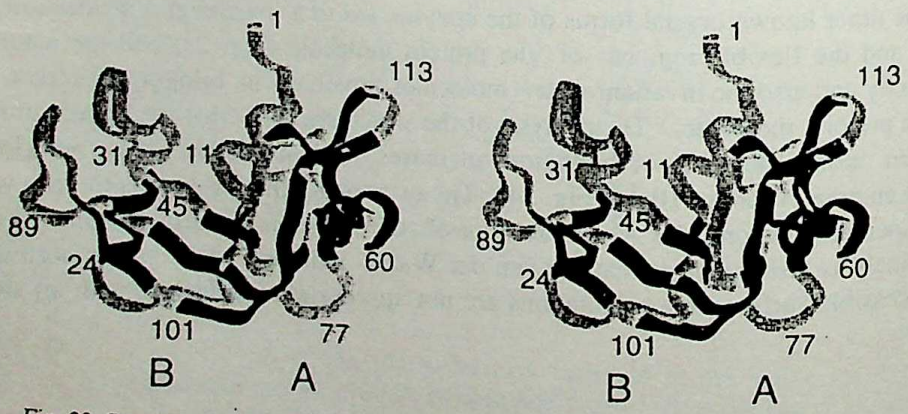

Fig. 23–Stereoview of the rigid (black) and the flexible (grey) regions of ribonuclease A.

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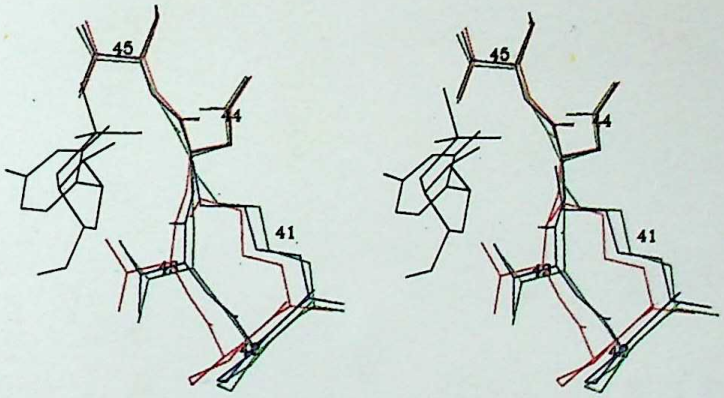

Fig. 22–Stereoview of residues 41-45 in the native form (green), the uridine vanadate complex (violet) and the 79% r.h. form (red) of ribonuclease A, after superposition of all C atoms.

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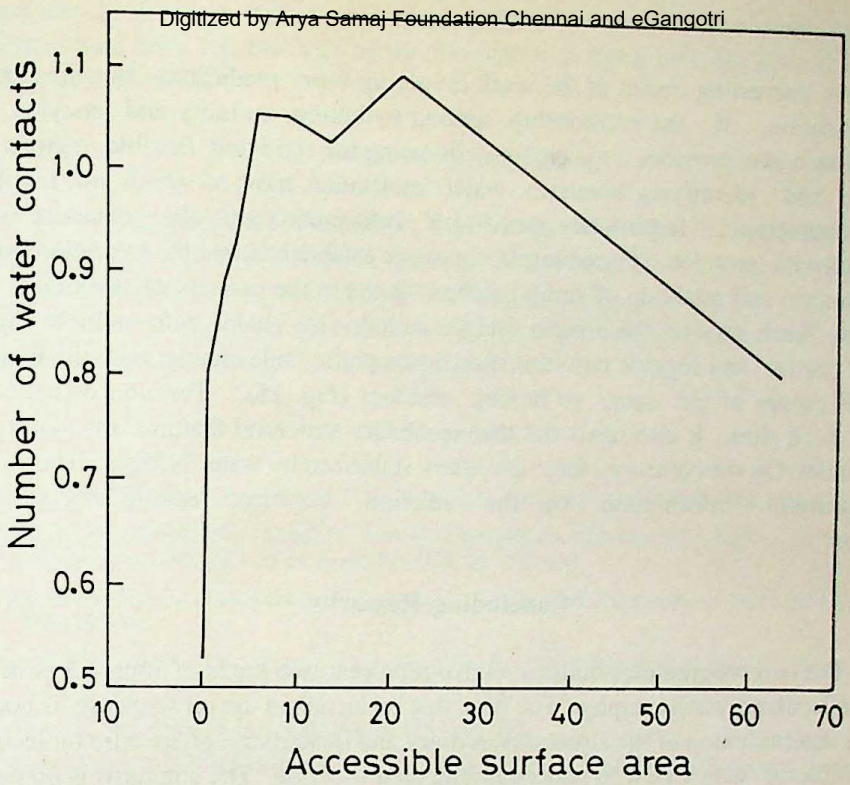

Fig. 24– Relation between accessible surface area and hydration in the atoms of the ribonuclease A molecule.

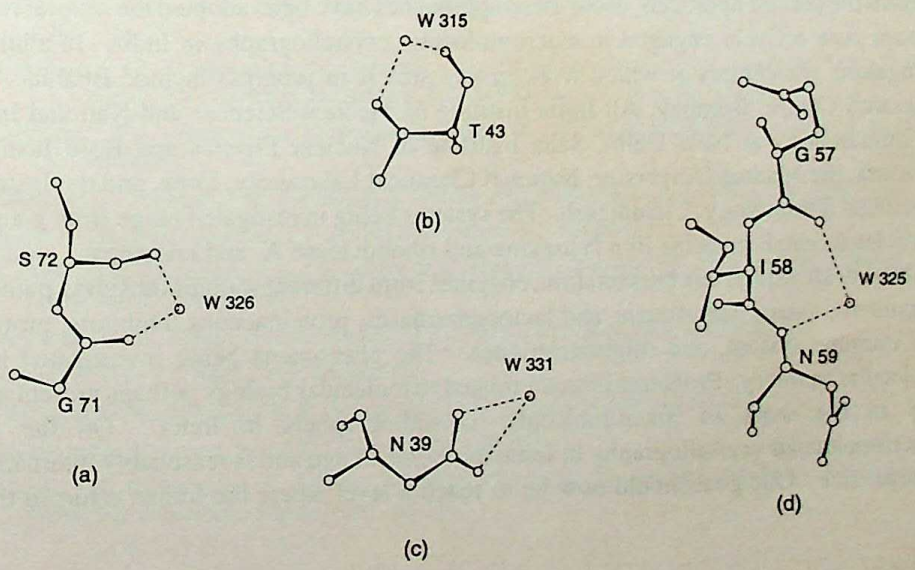

Fig. 25– Examples of favourable sites of hydration in a low humidity crystal form of lysozyme.

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An interesting result of the work involving water medicated transformations is the elucidation of the relationship among hydration, mobility and enzyme action. The approach also provides a means for delineating the rigid and flexible regions of the molecule and identifying invariant water molecules, most of which are involved in tertiary interactions. It provides significant information on the structure of water associated with proteins. For example, the work established that the hydration "shell" is discontinuous and made up of small patches. It led to the concept of favourable sites of hydration. Such sites on the protein surface include side chains with multiple hydrogen bonding centres, and regions between short hydrophilic side chains and the main chain O or NH groups of the same or nearby residues (Fig. 25). Terminii of helices also provide such sites. It also turns out that secondary structural features are not disrupted by hydration. On the contrary, they are often stabilized by water bridges. The work also provides useful information on the relation between atomic accessibility and hydration.

Concluding Remarks

The two programmes outlined above represent two kinds of approaches involving macromolecular crystallography. The first, that on lectins in the present case, is concerned with the determination of the structures, tertiary and quaternary, of specific molecules and their complexes, with a view to understanding their function. The emphasis is on particular molecules or family of molecules. The emphasis in the second is on a phenomenon, as in the programme on hydration and its consequences. Well established structures are often used in the second approach. Both these approaches have been adopted the several research groups now actively engaged in macromolecular crystallography in India. In addition to Bangalore, the centres at which work in this area is in progress include Bhabha Atomic Research Centre, Bombay, All India Institute of Medical Sciences and National Institute of Immunology at New Delhi, Saha Institute of Nuclear Physics and Bose Institute at Calcutta, the Madras University, National Chemical Laboratory, Pune, and the Institute of Microbial Technology, Chandigarh. The systems being investigated range from giant virus particles to small proteins like lysozyme and ribonuclease A, and encompass, in addition to those dealt with in this presentation, enzymes from different sources including pathogenic organisms, toxins, lactoferrins and lactoperoxidases, proteinaceous inhibitors, proteins of the immune system, and oligonucleotides. The phenomena being investigated include molecular mimicry. Problems directly related to molecular biology perhaps present a major gap in the work of macromolecular crystallographers in India. On the whole, macromolecular crystallography in India has come of age and is reasonably internationally competitive. Our goal should now be to reach a level where the Indian effort in the area

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is comparable to the very best in the world. Time and again Indian biophysicists and crystallographers have led the way in the international arena and this should not be an impossible goal to reach.

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